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SOIL GAS SENSING FOR DETECTION AND MAPPING OF VOLATILE ORGANICS

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The sensing of soil gas is a relatively new approach that shows great promise in assisting scientists in the detection and mapping of volatile organics in the subsurface. This document is an attempt at compiling all pertinent information on the current state of the art of soil gas sensing as it relates to the detection of subsurface organic contaminants. It is hoped that such a document will better assist all those individuals who are faced with assessing the extent of the contamination of our soil ground-water systems. Soil gas monitoring has been shown to be a cost effective means of delineating the size and movement of organic contaminants in the subsurface. It has also been shown to provide immediate information of the lateral extent of soil and ground-water contamination and to minimize and more accurately predict the number and location of conventional monitoring wells that must be drilled. As such, this document addresses five important areas related to soil gas monitoring; 1) site specific parameter considerations, 2) transport and retention of organics in soil and ground-water, 3) sampling methods, 4) analytical methods and 5) statistical treatment of soil organic vapor measurements.

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ABSTRACT

The sensing of soil gas is a relatively new approach that shows great promise in assisting scientists in the detection and mapping of volatile organics in the subsurface. This document is an attempt at compiling all pertinent information on the current state of the art of soil gas sensing as it relates to the detection of subsurface organic contaminants. It is hoped that such a document will better assist all those individuals who are faced with assessing the extent of contamination of our soil ground-water systems.

Soil gas monitoring has been shown to be a cost effective means of delineating the size and movement of organic contaminants in the subsurface. It has also been shown to provide immediate information of the lateral extent of soil and ground-water contamination and to minimize and more accurately predict the number and location of conventional monitoring wells that must be drilled. As such, this document addresses five important areas related to soil gas monitoring; 1) site specific parameter considerations, 2) transport and retention of organics in soil and ground-water, 3) sampling methods, 4) analytical methods and 5) statistical treatment of soil organic vapor measurements.

The document begins by outlining many of the parameters (water solubility, microbial influence, ground-water flow, etc.) that must be considered by the scientist before utilizing soil gas sensors in a field monitoring program. Next, the complex soil, air, water and hydrocarbon system is addressed with an overview of the important processes involved in the transport and fate of organic contaminants in the soil. Additional sections address the correct sampling and analytical methodologies for monitoring volatile organics in the subsurface, covering such sampling methods as headspace, ground probe, flux chamber and passive sampling techniques. Analytical methodologies covered outline the most appropriate methods to utilize for a given contaminant monitoring program. A statistical treatment of soil organic vapor measurements is also included to ensure that soil gas monitoring programs address the requirement for data precision. The statistical section also gives greater insight into understanding the spatial patterns of soil organic vapor measurements.

Finally, case studies are included to give the unfamiliar reader examples of the design, procedures and results of soil gas monitoring programs that have been successful in delineating the size and lateral extent of a subsurface organic contaminants.

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CHAPTER 1

INTRODUCTION

SOIL GAS SENSING FOR DETECTING AND MAPPING VOLATILE ORGANICS

Interest in the measurement of concentrations of volatile organic compounds in the pore-space gases of soil was stimulated by enactment of Superfund (the Comprehensive Environmental Response, Compensation, and Liability Act, or CERCLA) and by the November 1984 reauthorization of RCRA (the Resource Conservation and Recovery Act of 1976) which directed the EPA to promulgate standards for underground storage tanks to include provisions for leak detection. The applications discussed in this report are principally appropriate for the Superfund situation where contamination of the subsurface has occurred and must be assessed before taking remedial action: removal and biological treatment of the contaminated soil and ground water or both. In this case, the usual objective in measuring organic gases in soil is to map the lateral extent of soil and ground-water contamination or both while at the same time minimizing the number of conventional monitoring wells which must be drilled. Soil gas concentration serves as a surrogate for actual measurements of the concentrations of the compounds of interest in ground water. Maps of soil gas concentrations can be used to site ground-water monitoring wells more efficiently.

Volatile compounds are components in the soil and ground-water contamination at many, if not most, Superfund sites. Figure 1.1 shows the relationship between the number of volatile compounds and the number of organic priority pollutants found in a survey of ground-water monitoring data from 113 Superfund sites (Plumb, 1985). A regression line through these data shows a linear relationship with good correlation between the total number of volatile compounds and the total number of organic priority pollutants detected per site. Table 1.1 lists the 25 compounds most frequently reported at Superfund sites; 15 of these 25 are volatile organic solvents. In addition to whatever toxicity these volatiles may themselves possess, they may serve as tracers for other, non-volatile components provided that their gases arrive near the surface in measureable concentrations.

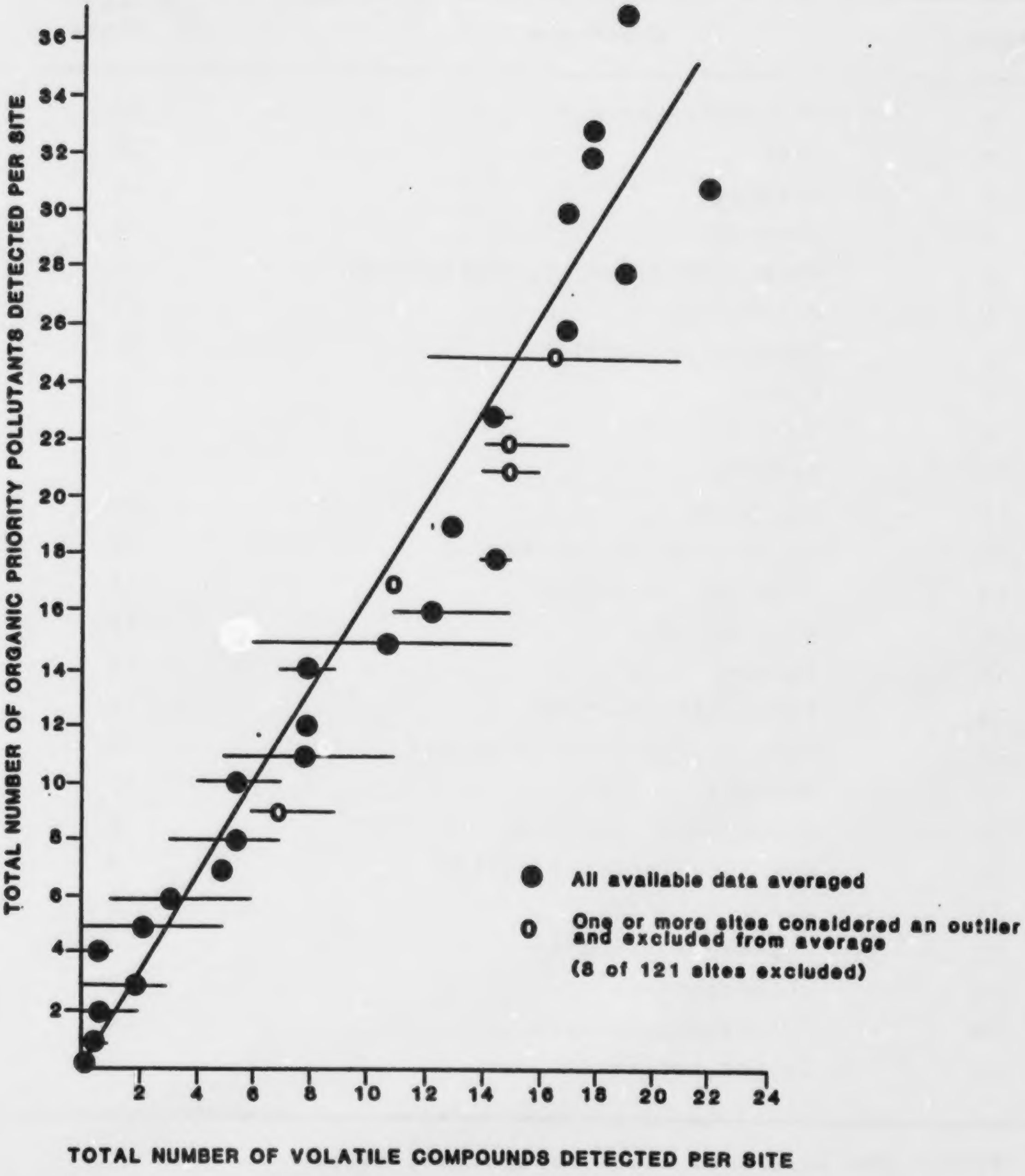

Figure 1.1. Relationship between number of volatile compounds and organic priority pollutants in ground-water in the vicinity of hazardous waste disposal sites (N= 113 sites) (Plumb, 1985).

TABLE 1.1. MOST FREQUENTLY REPORTED SUBSTANCES AT 546 NPL SITES

Rank	Substance	Percent of Sites
1	Trichloroethylene	33
2	Lead	30
3	Toluene	28
4	Benzene	26
5	Polychlorinated biphenyls (PCBs)	22
6	Chloroform	20
7	Tetrachloroethylene	16
8	Phenol	15
9	Arsenic	15
10	Cadmium	15
11	Chromium	15
12	1,1,1-Trichloroethane	14
13	Zinc and compounds	14
14	Ethylbenzene	13
15	Xylene	13
16	Methylene chloride	12
17	Trans-1,2-Dichloroethylene	11
18	Mercury	10
19	Copper and compounds	9
20	Cyanides (soluble salts)	8
21	Vinyl chloride	8
22	1,2-Dichloroethane	8
23	Chlorobenzene	8
24	1,1-Dichloroethane	8
25	Carbon tetrachloride	7

From: The Hazardous Waste Consultant, 1985.

Although the processes governing the movement of organics in the subsurface are discussed in detail in Chapter 2, a brief discussion of the process will illustrate the logic behind soil organic gas measurement. Figure 1.2 shows a subsurface cross-section immediately following a sudden, high-volume spill of an organic fluid. The spilled fluid has moved vertically downward through the unsaturated zone to form a lens on the water table (which has a specific gravity less than water) and has left behind a column of soil contaminated by residual product. The organic fluid lens will immediately begin to move under the force of gravity and to spread out on the water table. Under the conditions shown here, the lens will continue spreading until it eventually disappears, for all practical purposes. However, most petroleum fuels are a mixture of many compounds with a wide spectrum of properties such as molecular weight and water solubility. Some fraction of the compounds, generally quite small, will dissolve in ground water and will move downgradient with the ground-water gradient flow. Figure 1.3 shows the situation after the spill has stabilized days, weeks, or months after the occurance. The column of soil contaminated by residual product during the original spill remains. The lens of organic fluid has spread downgradient and is much thinner. The dissolved fraction of the spilled fluid is migrating with the ground-water flow. Gases from the spreading organic fluid lens have begun to move upward through the soil column above the path of the spreading organic plume. When the floating organic lens has disappeared, the volatile component dissolved in ground water will evolve from the ground water into the gases of the soil pore spaces.

In the situation where there exists a floating lens of free organic fluid, the initial concentration of organic gases above the lens can be estimated from its gas pressure. In the situation where there exists a small concentration of dissolved organic volatiles in ground water, the initial concentrations of volatile organics in the pore space gases immediately above the water table can be estimated from Henry's Law, as discussed at length in Chapter 2. Table 1.2 shows air:water concentration ratios measured for some common industrial solvents at room temperature (Thompson, 1984). From Table 1.2, we would expect a ground-water concentration of 26μg/ℓ of TCE to yield a pore-space gas concentration of 10μg/ℓ in the unsaturated zone immediately above the water table. These values must be regarded as rough approximations, but they illustrate the point that there are well-understood physical principles relating the concentrations of dissolved volatile organics in ground water to the pore space gas concentrations of these same volatiles.

The migration of the organic gases upward through the vadose zone is a complicated process, as discussed in Chapter

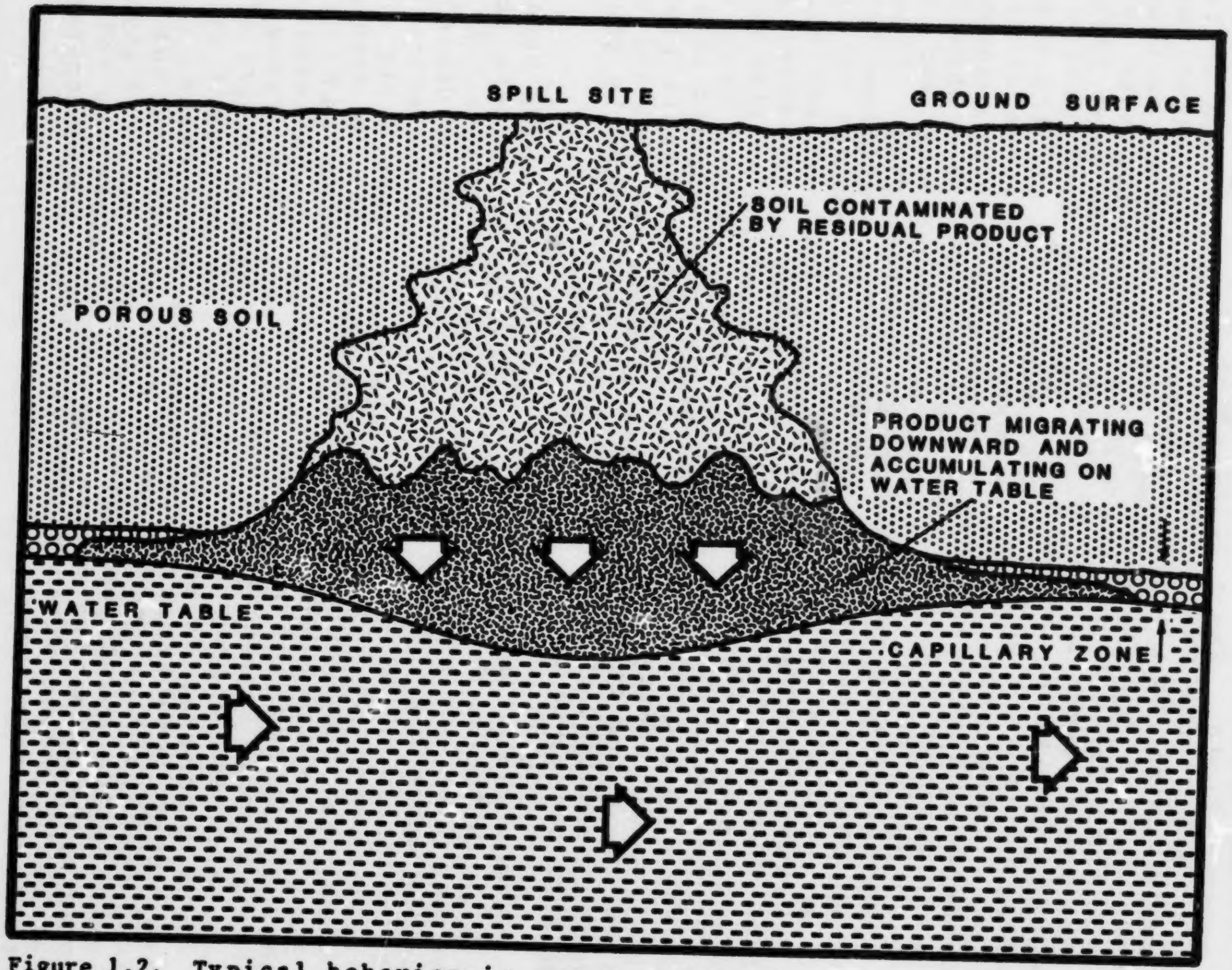
SPILL SITE
GROUND SURFACE
SOIL CONTAMINATED BY RESIDUAL PRODUCT
POROUS SOIL
PRODUCT MIGRATING DOWNWARD AND ACCUMULATING ON WATER TABLE
WATER TABLE
CAPILLARY ZONE

Figure 1.2. Typical behavior in porous soil following a sudden, high volume spill (NYDEC, 1984).

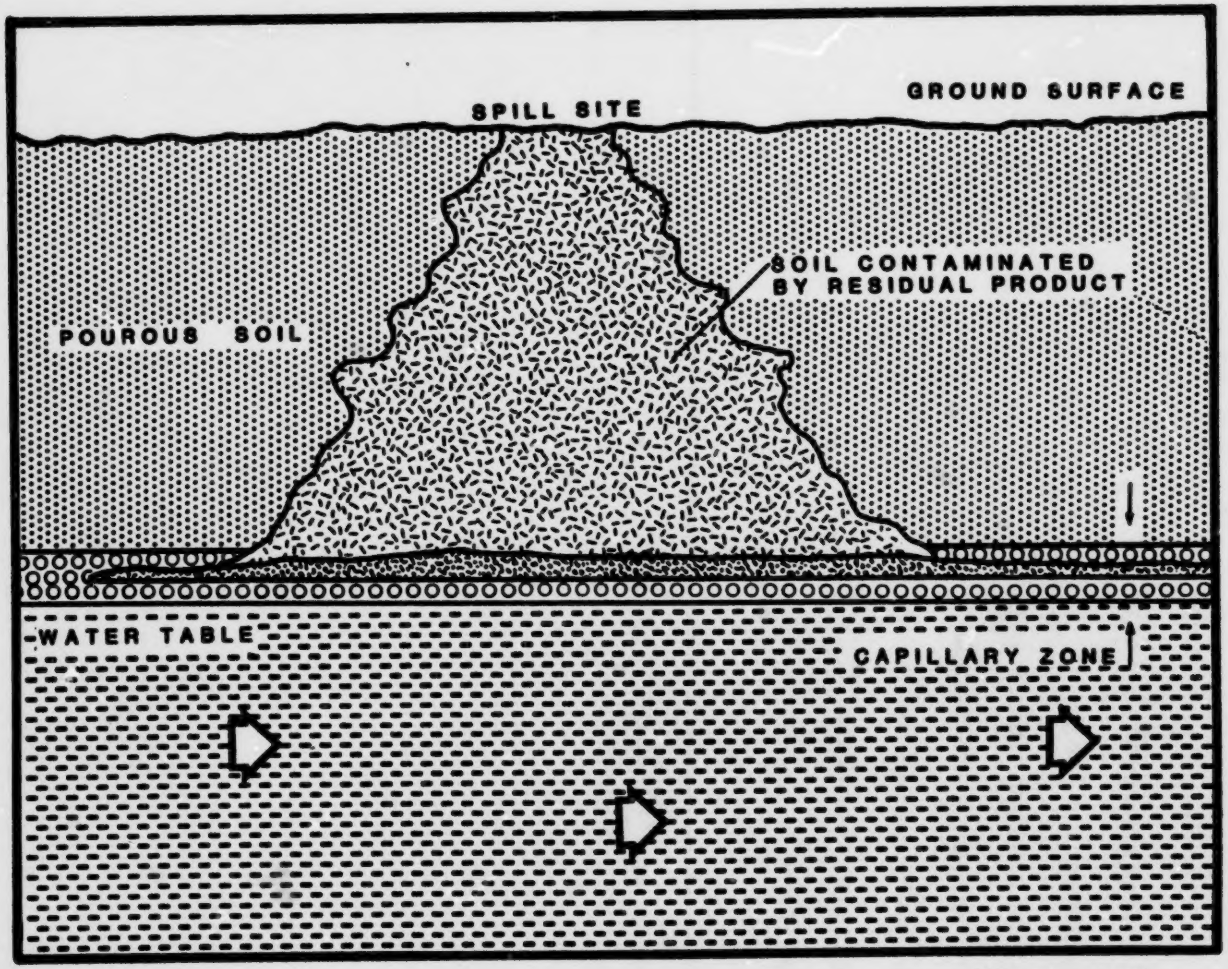
GROUND SURFACE
SPILL SITE
SOIL CONTAMINATED BY RESIDUAL PRODUCT
POUROUS SOIL
WATER TABLE
CAPILLARY ZONE

Figure 1.3. Behavior of product after spill has stabilized (NYDEC, 1984).

TABLE 1.2. AIR/WATER CONCENTRATION RATIOS FOR SOME COMMON INDUSTRIAL SOLVENTS AT 23^{0}C

Compound	Air: Water Ratio (μg/l of air:μg/l of water)
1,1 dichloroethylene (DCE)	1:1
1,2 transdichloroethylene	1:3
methylenechloride	1:12
1,1,1 trichloroethane (TCA)	1:15
trichloroethylene (TCE)	1:26
carbontetrachloride	1:1
tetrachloroethylene (PCE)	1:17
chloroform	1:9
F-113	4:1

(Marrin and Thompson, 1984)

2, but as a first-order approximation, it can be regarded as a diffusion process, represented by

$$\partial C/\partial t = D_o[\partial^2 C/\partial y^2]$$

where

C = soil gas concentration
t = time
D_o = diffusion coefficient
y = vertical distance above contaminant (or water table)

Confining discussion to "conservative" gases (where no chemical or biochemical processes add to or subtract from the pore space gases) and to a vertical cross-section in which the subsurface is homogeneous with uniform porosity and permeability in the unsaturated zone, it is possible to outline the qualitative nature of the expected vertical profiles of organic gas concentrations in soil gas. In the relatively simple situation where the evolution of the organic gases from the dissolved components in ground water has reached a quasi-steady state, this equation indicates that soil gas concentrations linearly decrease from the initial concentration immediately above the water table predicted by Henry's Law (or Table 1.2) to zero concentration at the soil surface. Figure 1.4 shows this situation schematically. Figure 1.5 is a vertical profile of carbon tetrachloride and chloroform above a ground-water contaminant plume in Nevada (Kerfoot and Barrows, 1986). The profile exhibits a linear decrease of concentration as the surface is approached. These experimental data, showing soil gas concentrations which increase linearly with depth, support the predictions of the steady state model. The subsurface vertical cross-section is rarely homogeneous, however; more often, a succession of strata is encountered in which there are varying permeabilities, porosities, soil types, and moisture contents. These varying properties influence the upward movement of organic gases and varying vertical gas concentration gradients.

Chemical and biochemical processes should also affect the vertical gas concentration profiles. Figure 1.6 contrasts the profiles of PCE and benzene reported from a site in northern California (Marrin and Thompson, 1984). The same rapid disappearance of benzene vapor with distance above the water table was reported in Nevada associated with the vertical profile of carbon tetrachloride and chloroform of Figure 1.5 (Kerfoot and Barrows, 1986). Apparently, different processes affect the movement of halocarbon gases such as tetrachloroethylene, dichloroethane and chloroform than affect non-halogenated hydrocarbons such as benzene. Several explanations for this differing behavior have been suggested,

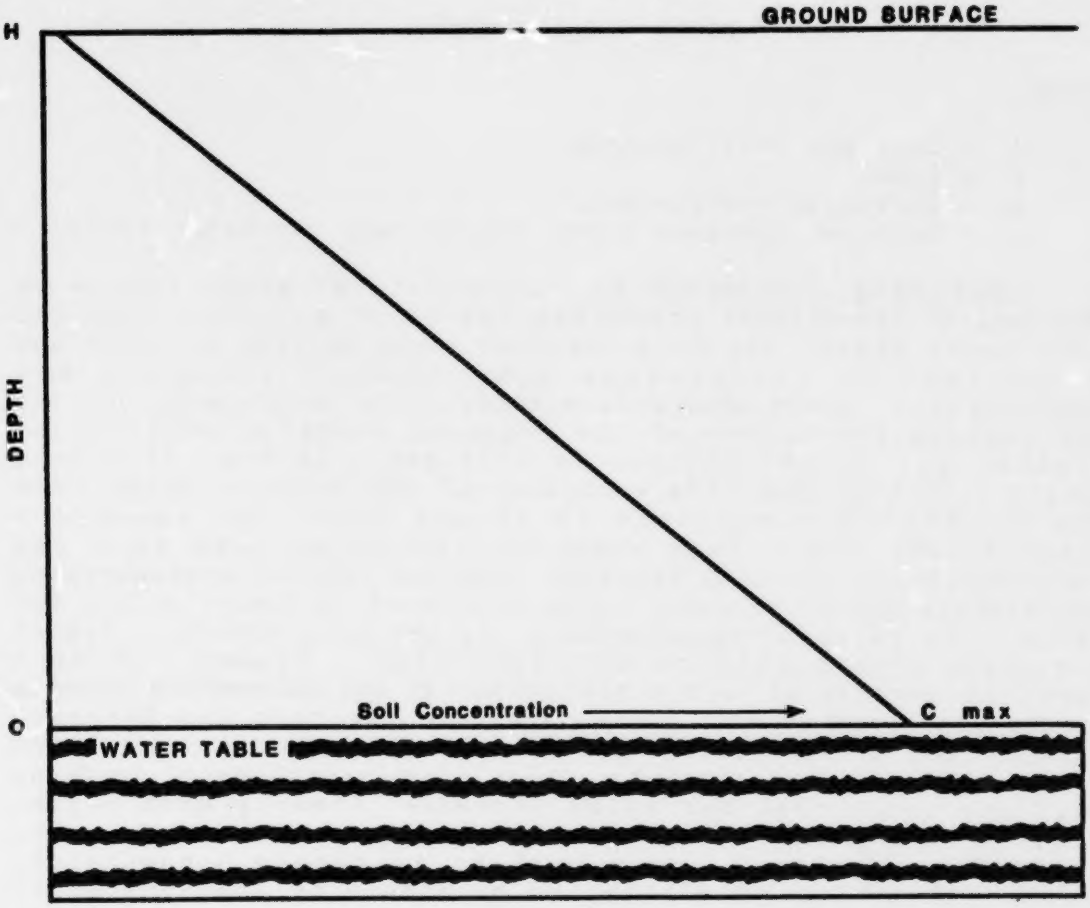
GROUND SURFACE
H
DEPTH
O
Soil Concentration
C max
WATER TABLE

Figure 1.4. Organic gas concentration distribution in the vadose zone expected from diffusion.

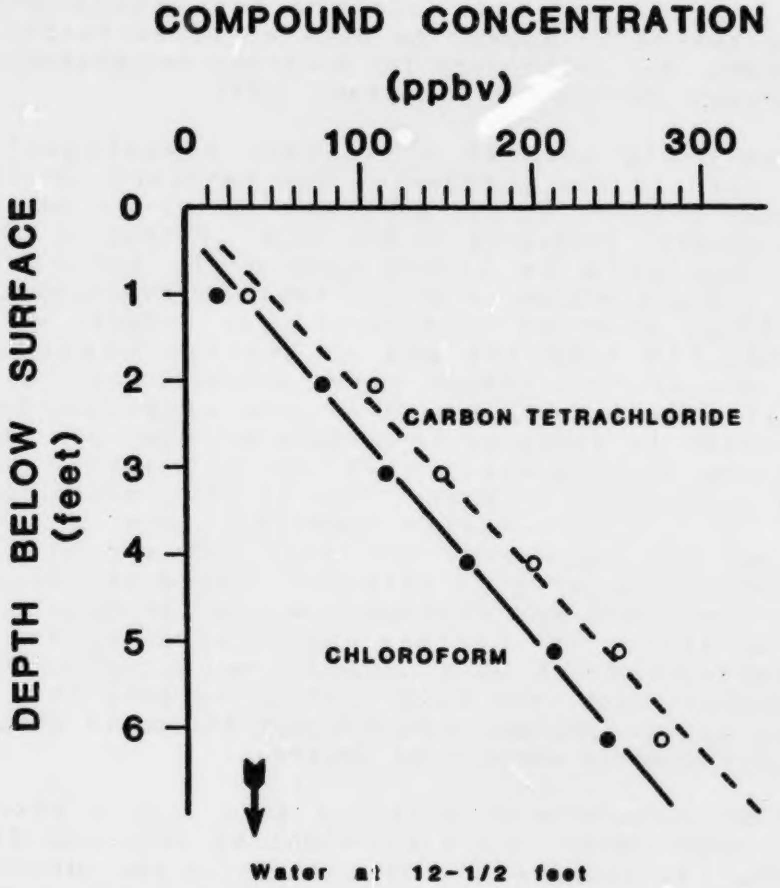

Figure 1.5. Chloroform and carbon tetrachloride depth distribution. Coefficient of determination (r^2 = .99) Kerfoot and Barrows, 1986).

including biological degradation, adsorption by organic matter and clays, and water solubility. Whatever the reason for the differing behavior of hydrocarbons and halocarbons, the halocarbons generally appear to behave "conservatively" and are, therefore, better tracers for soil-gas investigations than the hydrocarbons (Marrin and Thompson, 1984).

The basic approach in a soil-gas investigation at a particular site is now apparent. The vertical profiles of organic gases present in the soil pore spaces are measured and plotted for several locations at the site. Selection of tracer gases for the site is aided when prior information on contaminant concentrations in ground water is available. Based on the vertical profiles, the particular organic soil gases present, and the sampling and analytical methodologies available, one or more tracer gases are selected. A sampling depth is also selected, based on the measured vertical profiles, which is expected to produce soil gas concentrations well above the minimum concentrations detectable with the analytical techniques at hand. This is shown schematically on Figure 1.4. When this constant sampling depth is used, soil gas samples are collected and measured across the site preferably on a regular grid pattern. These values are then plotted on a map and are contoured either by hand or with a computer algorithm. The desired result is a contour plot of soil gas concentrations at a constant depth across the site; the investigator hopes that this plot is related in a more or less linear way to contaminant concentrations in ground water or in the buried waste stratum of interest.

Field measurements of soil gas have usually taken one of three basic approaches: (1) measurement of emission fluxes at the surface; (2) measurement of pore space gas concentrations at some depth in gas samples collected with subsurface probes or with shallow, temporary wells; or (3) use of passive collection devices buried at relatively shallow depths (Reid, 1985; Marrin and Thompson, 1984; Bisque, 1984; Manos, 1985; Kerfoot and Barrows, 1986; Spittler, 1985). These basic methods are listed in Table 1.3. The first two approaches involve collection of gas samples in the field for subsequent analysis; the third involves adsorption of the gas onto a collection medium such as activated charcoal: the adsorbed gas is later purged from the activated charcoal and is analyzed in the laboratory. With surface collectors and flux chambers and also with driven probes and temporary wells, gas samples can be collected with any of the techniques listed in Table 1.4. Figure 8.2 is a flow chart which describes the process of collecting and analyzing a soil gas sample with driven probes and temporary wells. Collection techniques include drawing samples with a gas chromatograph syringe directly from the sampling train,collection of gases by adsorption onto activated

TABLE 1.3. SOIL GAS MONITORING

Sampling Methods

- Driven probes
- Shallow "wells"
- Petrex tubes
- Collectors on surface
- Flux chambers

TABLE 1.4. SOIL GAS MONITORING

Collection Methods

- GC syringe
- Charcoal cartridge
- Stainless steel cannisters
- Tedlar or teflon bags

TABLE 1.5. ANALYTICAL METHODS FOR SOIL GAS SAMPLING

Method	Comment
Draeger tubes	very crude
Organic vapor analyzer	over 0.5 ppmv
Field GC	generally over 10 ppbv
Lab GC	can be less than 1 ppbv

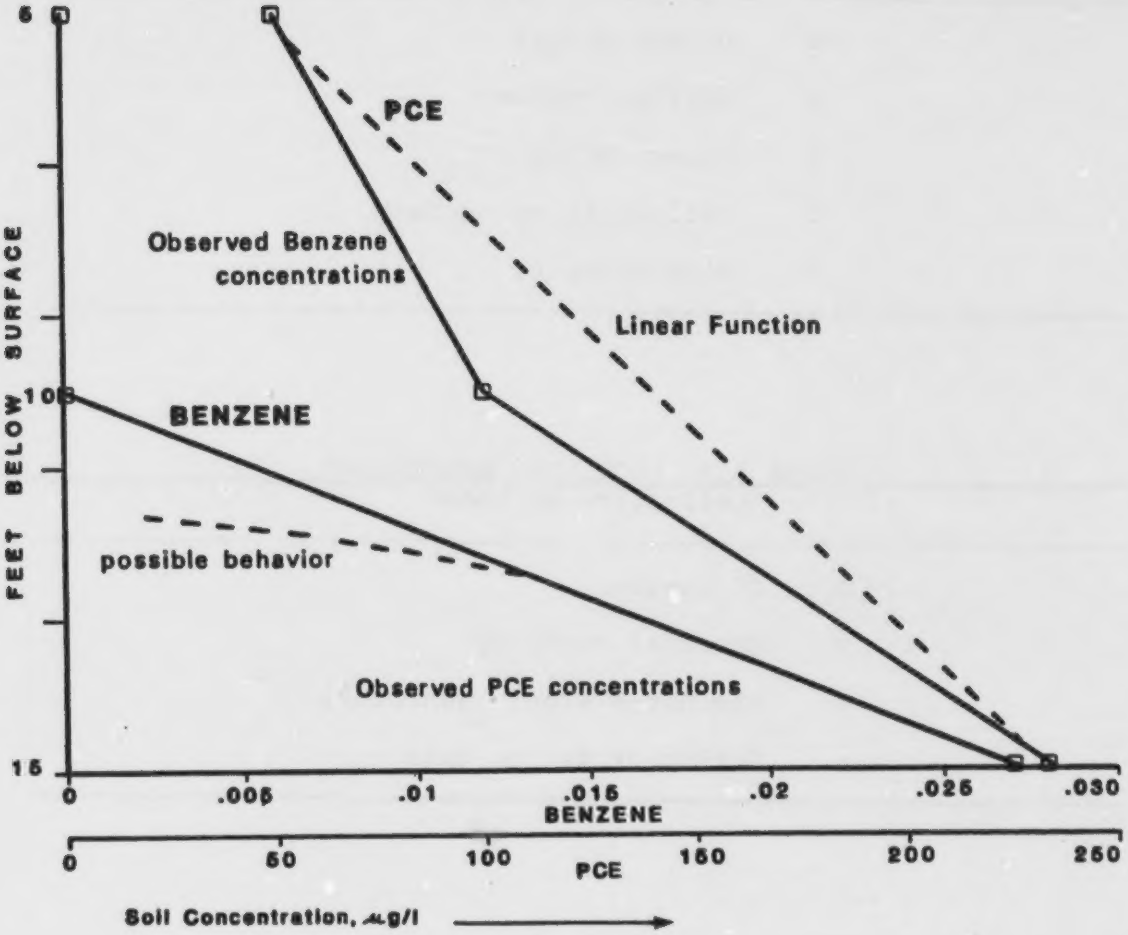

Figure 1.6. Soil-gas vertical profile at a site in northern California (Marrin and Thompson, 1984).

charcoal or Tenax from an airstream pumped from the probe or well, collection in stainless steel cannisters, and collection in Tedlar or Teflon bags.

Table 1.5 lists analytical methods which have been used in soil gas investigations. These include: (1) field measurements with either a portable organic gas analyzer (OVA) or with a transportable gas chromatograph, (2) laboratory gas chromatographic analysis of gas samples (via evacuated flasks or cannisters or teflon or teddar bags) or charcoal or Tenax cartridges collected in field, or (3) laboratory gas chromatograph/mass spectrometry (GC/MS) analysis of field samples. These methods are discussed in detail in Chapter 4. Another method which has been used in field measurements utilizes colorimetric devices usually called Draeger tubes. Table 1.5 also lists the usual minimum detectable concentrations associated with these various methods in practice. Draeger tubes are the least accurate and, usually, the least sensitive of the methods listed in Table 1.5. OVA's are also relatively insensitive and should not be expected to produce usable information where the total non-methane hydrocarbon concentrations are less than 0.5 ppmv. Transportable gas chromatographs have been used in field applications where individual gas species concentrations were greater than 10 ppbv (Barker, 1980).

Laboratory-based gas chromatography can reliably and economically measure individual gas species concentrations down to 1 ppbv; absolute detection limits are much smaller but such low concentrations are generally of little interest to soil gas surveys. The sensitivity and discriminative abilities of laboratory-based GC/MS measurements can extend down to concentrations considerably less than 1 ppbv; however, the substantial expense is rarely justifiable in soil gas investigations.

The range of gas measurement sensitivities listed in Table 1.5 means that soil gas measurements can detect very small concentrations of tracer gases. This sensitivity together with the specificity of the gas analyses gives soil gas investigations some important advantages over other indirect tools for ground-water investigations such as resistivity and other electrical geophysical techniques. The electrical techniques depend on the presence of substantial quantities of dissolved ionic solids in ground water to create detectable differences in aquifer conductivity between the contaminant plume and the surrounding unaffected areas. Detection and mapping contaminant plumes with electrical methods requires a significant conductivity contrast between contaminant plume and background as they are observed from the surface. A rule of thumb, sometimes quoted, suggests that a conductivity contrast of 1.5:1 or better is usually needed with a "shallow" aquifer (water table < 30 feet) to satisfactorily map a contaminant plume with electrical methods. This would require total dissolved solids concentrations in the plume to be at least 1.5 times the background TDS values. For deeply buried aquifers, the necessary contrast is higher because of the screening presence of the overburden. Not all Superfund sites have conductive contaminant plumes. Even in cases where such plumes exist, the contaminants of interest are usually organics which add little or nothing to ground-water conductivity. Because of these limitations, electrical techniques can be expected to "underdefine" contaminant plumes; plume outlines identified by electrical methods can be expected to be less extensive than the actual area of interest. Plume outlines defined with the most sensitive soil gas measurement techniques may tend to "overdefine" ground-water contaminant plumes because the organic gases rising from the ground-water plume will tend to spread laterally as they rise.

Soil-gas measurements have also been suggested as a means of detecting leaks from underground storage tanks; in this application the focus is on detecting leaking tanks before they become serious environmental problems. The EPA has estimated that the total number of underground storage tanks in the U.S. is in the neighborhood of 3,000,000 to 5,000,000 and that as many as 100,000 are leaking today while another 350,000 may leak within 5 years (Jeyapalan, et al., 1986; Hazardous Waste Report, 1984; Predpall, et al., 1984). Because measurement of volatile organic vapors in soil pore gas is probably the most sensitive known technique for detecting material leaked from underground storage tanks, the 1984 RCRA amendments have provoked considerable interest in such methods. The technical objectives of leak detection are distinct from those of site assessment. The goal in site assessment is to use soil-gas measurements as a surrogate for soil and ground-water sampling to map the lateral extent of contamination. The goal in leak detection is to provide an alarm when tank leak rates exceed a given value (current suggested maximum leak rates are 0.05 gallons/hr). To do this with soil-gas monitoring requires a known relationship between leak rates or volumes and soil-gas concentrations. As will be demonstrated, this relationship is highly site-specific. Other problems associated with leak detection by soil gas monitoring must be solved to make the technique workable. Among these problems are the following:

- New leakage must be detected in environments where soil already contains residual vapors from previous spills and leaks.

- No "action levels" exist to aid in deciding what soil gas concentrations should trigger remedial action.

- The relationships between ground-water concentrations of volatile organics and the resulting soil pore gas concentrations of those organics are very complex, and predictive models may require more data about a particular site than are likely to be available.

- Currently available measurement methods with adequate sensitivity may be too expensive for use as leak detectors.

While the problem of detecting leaks from underground storage tanks requires a different technology than does Superfund site assessment, the following discussions of gas vapor migration and current measurement technology should serve as a background for the development of leak detection methods.

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CHAPTER 2

SITE SPECIFIC PARAMETER CONSIDERATIONS

Because of the heterogeneous nature of soil and parent material found in the vadose zone, the movement of organic compounds in both the liquid and vapor phase are often difficult to predict with any degree of certainty (varying in both space and time). However, if the variability of site specific parameters is properly recognized, correct interpretations can be made. This chapter covers the significance of the parameters listed in Table 2.1. Special attention will be given to the parameter influence on soil gas monitoring and on contaminant plume detection in the saturated zone.

CHEMICAL AND PHYSICAL PROPERTIES OF THE ORGANIC COMPOUND

(1) Vapor pressure: The pressure of the vapor of a liquid confined such that the vapor collects above it is referred to as the vapor pressure. Thus, at spill sites,organic compounds with high vapor pressures would be expected to be present to some degree in the vapor phase of soil pores. Highly volatile fuels such as gasoline are known to evaporate relatively fast even in the subsoil, forming an envelope of hydrocarbon vapors around the core of the spill (Schwille, 1975). If an organic compound has an exceedingly low vapor pressure (e.g., pesticides), it would not be a good candidate for soil vapor monitoring. A list of the vapor pressures of many organic compounds can be found in Table 2.2, compiled by Mackay and Shiu (1981).

(2) Water solubility: The extent to which an organic compound (solute) dissolves in a solvent (water), is referred to as the water solubility of the compound. Organic compounds with high water solubility would be expected to partition primarily into the liquid water phase. The rate at which these compounds would move through the unsaturated zone would therefore be controlled to a great extent by the unsaturated hydraulic conductivity of

TABLE 2.1. SITE SPECIFIC PARAMETER CONSIDERATIONS

A. Chemical and Physical Properties of the Organic Compound.

1) Vapor pressure
2) Water solubility
3) Henry's law constant
4) Concentration
5) Organic carbon distribution coefficient (K_{oc})
7) Density
8) Viscosity
8) Dielectric constant
9) Boiling point
10) Molecular weight

B. Properties of the Unsaturated Zone.

1) Air filled porosity
2) Volumetric water content
3) Soil organic matter
4) Soil texture
5) Vapor pressure of water in the soil pores
6) Shape and size of pores
7) Depth of unsaturated zone
8) Retention
9) Temperature and temperature gradients
10) Microbial influence

C. Hydrogeologic Properties

1) Ground water flow (direction, velocity, gradient)
2) Water table oscillations
3) Lithology of the aquifer

D. Characteristics of the Spill

E. Miscellaneous

1) Rainfall
2) Background water quality
3) Barometric pressure and wind
4) Proximity to rivers, lakes and pumping wells.

TABLE 2.2. PHYSICAL AND CHEMICAL PROPERTIES OF VARIOUS ORGANIC COMPOUNDS

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure P, kPa*	Solubility S, g/m^{3}	Henry's law constant kPa m^{3}/mol^{a} calc	exptl	recom
Data at 25^{o}C for gaseous alkanes								
Methane	16.04	-182.5	-164	27260	24.1	67.4		67.4± 2.0
Ethane	30.7	-183.3	- 88.6	3990	60.4	50.6		50.6± 1.1
Propane	44.11	-189.7	- 42.1	941	62.4	71.6		71.6± 2.4
n-Butane	58.13	-138.4	- 0.5	243	61.4	95.9		95.9± 4.1
Isobutane	58.13	-159.6	- 11.7	357	48.9	120		120± 5.2
2,2-Dimethyl-propane	72.15	- 16.6	9.5	172	33.2	373		373± 11.2
Data at 25^{o}C for liquid alkanes								
n-Pentane	72.15	-129.7	36.1	68.4	38.5	128		125±10
					39.5	125		
					40.0	123		
					40.4	122.2		
					47.6	103.7		
Isopentane	72.15	-159.9	27.9	92.6	47.8	140		138±5
					48.0	139		
					49.6	134.7		
n-Hexane	86.17	- 95	68.95	20.2	9.5	190		170±25
					9.47	191		
					9.52	190		
					12.3	147		
					12.4	144		
					16.2	110		
					18.3	98.9		

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure p, kPa*	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
2-Methyl-pentane	86.17	-153.7	60.3	28.2	13.8	175.		170±15
					13.0	186		
					15.7	154		
3-Methyl-pentane	86.17		63.3	25.3	12.8	172		172±8
					13.1	171		
2,2-Dimethyl-butane	86.17	- 99.9	49.7	42.6	18.4	199		173±16
					21.2	173		
					23.8	154		
2,3-Dimethyl-butane	86.17	-128.5	58.0	31.3	19.1	141		130±10
					22.5	120		
n-Heptane	100.21	- 90.6	98.4	6.11	2.93	209		230±50
					2.24	273		
					2.66	230		
					2.19	280		
					3.37	182		
2-Methyl-hexane	100.21	-118.3	90.0	8.78	2.54	346		346±21
3-Methyl-hexane	100.21	-119	92	8.21	2.64	312		240±75
					4.95	166		
2,2-Dimethyl-pentane	100.21	-123.8	79.2	14	4.40	318		318±8
2,3-Dimethyl-pentane	100.21		89.8	9.18	5.25	175		175±7

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
2,4-Dimethylpentane	100.21	-119.2	80.5	13.1	4.06	323		300±25
					4.41	298		
					5.50	239		
3,3-Dimethylpentane	100.21	-134.5	86.06	11.0	5.94	186		186±10
n-Octane	114.23	- 56.23	125.7	1.88	0.66	325		300±50
					0.431	499		
					0.493	438		
					0.85	253		
					0.88	244		
3,Methylheptane	114.23	-120.5	115	2.6	0.792	376		376±15
2,2,4-Trimethylpentane	114.23	-107.4	99.2	6.56	2.44	308		330±30
					2.05	365		
2,3,4-Trimethylpentane	114.23	-109.2	113.5	3.60	1.36	302		190±15
					2.30	179		
2,2,5-Trimethylhexane	128.26	-105.8	124.1	2.21	1.15	219		350±120
					0.54	467		
n-Nonane	128.26	- 51	150.8	0.571	0.122	601		500±200
					0.098	748		
					0.22	333		

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a		
						calc	exptl	recom
4-Methyl-octane	128.26	-113.2	142.4	0.903	0.115	1010		1000±100
n-Decane	148.28	- 29.7	174.1	0.175	0.052	500		700±300
					0.024	1080		
Undecane	156.32	- 25.59	195.9	0.0522	0.044	185		1855±760
Dodecane	170.33	- 9.6	216.3	0.0157	0.0034	723		750±250
					0.0037	786		
					0.00844	317		
Tetradecane	190.38	5.86	253.7	0.00127	0.00606	34.7		
					0.0022	110		
				0.00124				
Hexadecane	226.44	18.17	287	0.0000898	0.00628	3.24		
					0.0009	22.6		
				0.000917				
Data at 25^{o}C for solid alkanes								
Octadecane	254.4	28.18	316.1	7.44×10^{-6a}	0.0021	0.84		
				1.30×10^{-5a}		1.463		
				2.59×10^{-5a}		2.92		
				6.92×10^{-6b}				
					0.00608			
Eicosane	282.6	36.8	343	2.18×10^{-7a}	0.0019	0.025		
				2.67×10^{-6a}		0.288		
				1.58×10^{-7b}				

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure P, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
Hexacosane	366.7	56.4	412.2	7.32x10^{-12a} 3.55x10^{-12b}	0.0017	7.7x10^{-7}		

[a] Extrapolated value from liquid state.

[b] Calculated from the extrapolated vapour pressure with a fugacity ratio correction.

Data at 25^{o}C for cycloalkanes

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure P, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
Cyclopentane	70.14	- 93.88	49.26	42.4	156 160	19.1 18.6		18.5±1.1
Cyclohexane	84.16	6.55	80.7	12.7	55 57.5 66.5	19.4 18.6 16.1		18.0±2.0
Methyl-cyclopentane	84.16	-142.14	71.8	18.3	42 41.8	36.7 36.8		36.7±1.4
Methyl-cyclohexane	98.19	-126.6	100.9	6.18	14 16	42.8 38.0		40±3.0
1-cis-2-Dimethylcyclohexane	112.2	- 50.1	129.7	1.93	6.0	36.1		38±5.0
1,4,-trans-Dimethyl-cyclohexane	112.2	- 37	119.4	3.02	3.84	88.2		88.2±4.0
1,1,3-Trimethylcyclopentane	112.3	- 14.2	104.9	5.3	3.73	159		159.±8

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
Propylcyclo-pentane	112.2	-117.3	103.0	1.64	2.04	90.2		90.2±4.4
Pentylcyclo-pentane	140.26	- 83		0.152	0.115	185		185±18
Data at 25°C for gaseous alkenes								
Ethene	28.5	-169.2	-103.7	6070	131	21.7		21.7±2.0
Propene	42.08	-185.3	- 47.4	1140	200	21.3		21.3±3.0
1-Butene	56.12	-185.4	- 6.3	297	222	75		75±4.0
2-Methyl-propene	56.12	-140.4	- 6.9	304	263	64.8		64.8±6
3-Methyl-1-butene	70.14	-168.5	20.0	120	130	54.7		54.7±6
[a]Calculated using atmospheric pressure.								
Data at 25°C for liquid alkenes								
1-Pentene	70.14	-138	30.0	85	148	40.3		40.3±2.0
2-Pentene	70.14	-151.4	36.9	66	203	22.8		22.8±1.0
1-Hexene	84.16	-139.8	63.4	24.8	50	41.8		41.8±1.0
2-Methyl-1-pentene	84.16	-135.7	60.7	26.0	78	28.1		28.1±1.2

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
4-Methyl-1-pentene	84.16	-153.6	53.9	36.1	48	63.2		63.2±3.5
2-Heptene (trans)	98.19	-136.6	95.7	6.45	15	42.3		42.3±4.0
1-Octene	112.2	-101.7	121.3	2.32	2.7	96.4		96.4±7.1
Data at 25°C for dienes								
Butadiene	54.09	-108.9	- 4.4	281	735	7.46^a		7.46±0.2
2-Methyl-1,3-butadiene	68.13	-146	34	73.3	642	7.78		7.78±0.12
1,4-Pentadiene	68.13	-148.3	26	98	558	12.0		12±0.6

[a] Calculated using atmospheric pressure.

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
Data at 25°C for alkynes								
Propyne	40	- 101	- 23.2	558	3640	1.11^a		1.11±.04
1-Butyne	50.09	-125.7	8.1	188	2870	1.91^a		1.91±0.07
1-Pentyne	68.13	- 90	40.18	57.6	1570	2.5		2.5±.05

[a] Calculated using atmospheric pressure.

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
Data at 25^{o}C for monoaromatics								
Benzene	78.11	5.53	80.1	12.7	1780	0.557	0.562	0.550$\pm$.025
					1755	0.565		
					1769	0.561		
					1790	0.554		
					1779.5	0.557		
					1740	0.570		
					1869	0.533		
					1770	0.560		
Toluene	92.13	-95	110.6	3.80	515	0.68	0.673	0.670$\pm$.035
					517	0.677		
					544	0.632		
					534.3	0.655		
					500	0.70		
					519.5	0.674		
					627	0.558		
Ethyl-benzene	106.2	-95	136.2	1.27	152	0.887	0.854	0.80$\pm$.07
					177	0.762		
					131	1.03		
					208	0.648		
					161	0.837		
					175	0.771		
p-Xylene	106.2	13.2	138	1.17	185	0.671		0.710$\pm$.08
					198	0.628		
					157	0.791		
					156	0.797		
					200	0.621		

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
m-Xylene	106.2	- 47.9	139	1.10	162	0.721		0.700±0.10
					196	0.596		
					173	0.675		
					146	0.80		
					134	0.872		
o-Xylene	106.2	- 25.2	144.4	0.882	175	0.535		0.50±0.06
					170.5	0.549		
					167	0.561		
					204	0.459		
					213	0.440		
1,2,3-Trimethylbenzene	120.2	- 25.4	176.1	0.202	75.2	0.323		0.323±0.02
1,2,4-Trimethylbenzene	120.2	- 43.8	169.4	0.271	57	0.571		0.590±.04
					51.9	0.627		
					59	0.552		
1,3,5-Trimethylbenzene	120.2	- 44.7	164.7	0.328	97.0	0.407		0.60±.20
					48.2	0.818		
Propylbenzene	120.2	-101.6	159.2	0.449	55	0.981		0.700±.30
					120	0.450		
Isopropylbenzene	120.2	- 96.6	154.2	0.611	50	0.147		0.130±.025
					48.3	0.152		
					65.3	0.112		

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^oC	bp, ^oC	Vapor pressure p, kPa*	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
1-Ethyl-2-methyl-benzene	120.2	- 80.8	165.2	0.330	93.05	0.427		0.427±.025
1-Ethyl-4-methyl-benzene	120.2	- 62.4	162	0.393	94.85	0.498		0.498±.03
n-Buytyl-benzene	134.2	- 88	183	0.137	12.6	1.46		1.30±.25
					11.8	1.56		
					15.4	1.04		
					17.7	1.04		
					50.0	0.368		
Isobutyl-benzene	134.2	- 51.4	172.8	0.248	10.1	3.30		3.30±.13
s-Butyl-benzene	134.2	- 75.5	173	0.241	17.6	1.84		1.40±.40
					30.9	1.05		
t-Butyl-benzene	134.2	- 57.8	169	0.286	34.0	1.13		1.20±0.10
					29.5	1.30		
1,2,4,5-Tetra-methylbenzene	134.2	- 79.2	196.8	0.0659	3.48	2.54		2.54±0.20
1-iso-Propyl-4-methylbenzene	134.2	- 67.9	177.1	0.204	34.15	0.80		0.80±.10

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
n-Pentyl-	148.25	- 75.0	205.4	0.0437	10.5	0.62		0.60±.06
Data for polynuclear aromatics at 25^{o}C								
Naphthalene	128.19	80.2	218	1.09×10^{-2}	34.4	0.0407	0.0489	0.0430±.004
					31.2	0.0448		
					31.7	0.0441		
					33.5	0.0417		
					31.3	0.0446		
					30.8	0.0454		
					1.69	0.0441		
					30.0	0.0466		
					22.0	0.0635		
				1.04×10^{-2}				
				1.16×10^{-2}				
				3.11×10^{-2a}				
				1.08×10^{-2a}				
1-Methyl-naphthalene	142.2	- 22	244.6	8.84×10^{-3}	28.5	0.0041	0.0263	0.0450±.004
					30.0	0.0419		
					25.8	0.0487		
					29.9	0.0420		
				7.90×10^{-3a}				
				7.17×10^{-3a}				
2-Methyl-naphthalene	142.2	34.6	241.1	9.03×10^{-3a}	25.4	0.0405		
				7.24×10^{-3b}	24.6	0.0419		
				9.07×10^{-3a}				
1-Ethyl-naphthalene	156.2	- 13.8	258.7	2.51×10^{-3a}	10.7			
					10.0			

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
2-Ethyl-naphthalene	156.2	liquid		4.21×10^{-3}	8.0	0.0822		
				3.24×10^{-3a}				
Biphenyl	154.21	71	255.9	1.30×10^{-3}	7.48	0.0268	0.0413	0.028±.002
					7.0	0.0286	0.0304	
					7.45	0.0269		
					7.50	0.0267		
					7.08	0.0283		
					5.94	0.0337		
					3.87	0.0518		
				5.80×10^{-4}				
				3.92×10^{-3a}				
				7.55×10^{-3a}				
Acenaphthene	154.21	96.2	277.5	3.07×10^{-3a}	3.88	0.0237	0.0148	0.024±.002
				5.96×10^{-4b}	3.93	0.0234	0.0157	
					3.47	0.0265		
				4.02×10^{-3a}				
Fluorene	166.2	116	295	8.86×10^{-5c}	1.90	0.00775	0.0101	0.0085±.002
					1.98	0.00744		
				1.13×10^{-2a}				
				1.66×10^{-3a}				
Phenanthrene	178.23	101	339	2.67×10^{-5c}	1.18	0.00403	0.00398	0.0040±.0008
					1.07	0.00445	0.00365	
					1.29	0.00367		
					1.60	0.00297		
					1.15	0.00414		
					1.002	0.00475		

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^{o}C	bp, ^{o}C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
				$2.27x10^{-5c}$				
				$1.59x10^{-4a}$				
				$4.64x10^{-4a}$				
Anthracene	178.23	216.2	340	$1.44x10^{-6c}$	0.075	0.0034	0.073	0.0060±.003
					0.073	0.0034	0.676	
					0.041	0.0063		
					0.046	0.0056		
					0.030	0.0085		
				$8.32x10^{-7c}$				
				$3.17x10^{-5a}$				
				$1.44x10^{-4a}$				
Pyrene	202.3	156	360	$8.86x10^{-7c}$	0.148	0.00121	0.0011	0.0012±.002
					0.135	0.00133		
					0.132	0.00136		
					0.175	0.00102		
					0.171	0.00105		
Fluorathene	202.3	111	375	$1.79x10^{-3a}$	0.260	0.198		0.22±.03
				$2.54x10^{-4b}$	0.265	0.194		
					0.206	0.249		
					0.236	0.219		
1,2-Benzanthracene	228.3	160		$6.67x10^{-13}$ (20°)	0.014			
					0.01			

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, ^oC	bp, ^oC	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
3,4-Benzo-pyrene	252.3	175		6.67×10^{-13}	0.0012	1.4×10^{-7}		
					0.0038	4.43×10^{-8}		
					0.0040	4.21×10^{-8}		

^{a}Extrapolated values from liquid state.
^{b}Calculated from the extrapolated vapor pressure with a fugacity ratio correction.
^{c}Extrapolated from solid vapor pressure.

Data for halogenated alkanes and alkenes at 25°C unless otherwise stated.

Compound	MW	mp, ^oC	bp, ^oC	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
Chloromethane	50.5	-97.7	-24.2	570	5350	0.951^a		0.95±.05
				480(20°)	7400(20°)	0.691^a (20°)	0.731 (20°)	
					6270(20°)	0.817^a (20°)		
				499(20°)	7250(20°)	0.706^a (20°)		
Dichloro-methane	84.9	-95.1	39.7	58.40	19400	0.256	0.272	0.26±.02
					13200			
				46.53 (20°)	13200(20°)	0.299 (20°)	0.301	
				48.31 (20°)				
				21.08 (1.5°)	22700(1.5°)	0.079 (1.5°)		
Trichloro-methane	119.4	-63.5	61.7	25.60	7900	0.387	0.322	0.38±.03
					7950	0.383		
				32.80 (20°)	8000(20°)	0.496 (20°)		

(continued)

TABLE 2.2 (continued)

Compound	MW	mp,°C	bp,°C	Vapor pressure p, kPa*	Solubility S,g/m^3	Henry's law constant kPa m^3/mol^a		
						calc	exptl	recom
				20.06	8200(20	0.292	0.283	
				(20°)		(20°)	(20°)	
				8.8	10300(1.5°)	0.102		
				(1.5°)		(1.5°)		
Carbon	153.8	-22.9	76.5	15.06	1160	1.586	2.16	2.0±0.4
tetrachloride					800	2.895		
				12.13	800(20°)	2.331		2.30±.2
				(20°)		(20°)		(20°)
				12.0	785(20°)	2.351	2.21	
				(20°)		(20°)	(20°)	
Chloroethane	64.9	-136.4	12.27	100.7	5710(20°)	1.145		(.20±.20
				(20°)		(20°)		(20°))
					4700(20°)	1.391		
						(20°)		
1,1-Dichloro-	98.97	-96.98	57.5	30.10	5100	0.585		0.58±.02
ethane				24.42	5500(20°)	0.439		
				(20°)		(20°)		
1,2-Dichloro-	98.97	-35.36	83.47	10.93	8700	0.124	0.099	0.11±.01
ethane				8.52	8800	0.096		
				8.40	8000	0.104		
				8.93	8000(20°)	0.111		
						(20°)		
1,1,1-Tri-	133.4	-30.4	74.1	16.53	720	3.06		2.8±.04
chloroethane				13.20	730(20°)	2.41	3.47	
				(20°)		(20°)	(20°)	
				13.33	950(37°)			
				(20°)				

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a		
						calc	exptl	recom
				12.80 (20°) 5.33 (1.5°)	480(20°) 880(1.5°)	3.56 (20°) 0.808 (1.5°)		
1,1,2-Tri chloroethane	133.4	-36.5	113.8	4.04 3.30 (20°)	4420 4500(20°)	0.122 0.8978 (20°)		0.12±02
1,1,1,2-Tetra-chloroethane	167.85	-70.2	130.5	1.853	1100	0.283		0.28±.02
1,1,2,2-Tetra-chloroethane	167.85	-36	146.2	0.867 0.647(20°)	3000 3200	0.0485 0.0455		0.048±.04
1,1,2,2,2-Pentachloro-ethane	202.3	-29	162	0.60 0.444(20°)	480 500 (20°)	0.253 0.180(20°)		0.22±.04
Hexachloro-ethane	236.7	-	186	0.044 0.028(20°)	8 50 (22°)	1.302		
Vinylchloride	62.5	-153.8	-13.4	344(20°) 308(20°)	2700 90 (20°) 60 (10°)	2.35^d 70.4(20°)^d 105.6(10°)^d	117.6 (10°)	

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa*	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
1,1-Dichloro-ethene	96.94	-122.1	37	79.73	400	13.32		
				66.0(20°)	5500 (20°)	1.16 (20°)	15.61 (20°)	
1,2-Dichloro-ethene (cis)	96.94	-80.5	60.3	27.46	3500	0.761		
1,2-Dichloro-ethene (trans)	96.94	-50	47.5	43.47	6300	0.669		
				34.65(20°)	300 (10°)			
1,1,2-Tri-chloroethene	131.4	-73	87	9.87	1100	1.179		
					1000	1.30		
				7.86(20°)	1100 (20°)	0.939 (20°)	0.904 (20°)	
				8.0(20°)				
				3.27 (1.5°)	1000 (1.5°)	0.430 (1.5°)		
Tetrachloro-ethene	165.83	-19	121	2.48	140	2.94	1.239	2.3±.4
					400	1.03		
				1.90(20°)	120 (20°)	2.62 (20°)	2.03 (20°)	
				1.80(20°)	150 (20°)	1.99 (20°)		
				0.64(1.5°)	130 (1.5°)			
Trichloro-propane	147.5	-14.7	156.9	0.413	1900 (20°)			

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
3-Chloro-propane	76.53	-134.5	45	48.13	3370 3000	1.09 1.228		1.10±0.1
1-Chloro-2-methyl-propane	92.57	-131	68	12.06	9164	0.122		0.12±.01
2,3-Dichloro-propane	110.97		94	7.06	2150	0.365		0.36±.04
1,3-Dichloro-propane (cis)	110.97		104.3	5.735	2700	0.236		0.24±.03
1,3-Dichloro-propane	110.97		112	4.53(20°)	2800 (20°)	0.18 (20°)		0.18±.02 (20°)
1,2-Dibromo-methane	187.9	-34.2	167.3	0.271	1696	0.0322		0.032±.003
Bromoform	252.75	-8.3	149.5	0.747 0.719	3033 3190 (30°)	0.0623		0.062±.006
Fluorotri-cloromethane	137.37		23.8	88.5(20°)	1100 (20°)	11.05 (20°)	81.20 (20°)	
Difluorodi-chloromethane	120.91	-158	-29.8	573(20°)	280	43.75^d	40.60	

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa*	Solubility S, g/m^3	Henry's law constant kPa m^3/mol[a]		
						calc	exptl	recom
Bromomethane	94.94	-93.6	3.56	183.9	18040 (20°)	0.533(20°)[d]		
Fluoromethane	34.03	-141.8	-78.4	3536	1770 (30°)	1.95(30°)[d]		
Data for halogenated aromatics at 25°C								
Chlorobenzene	112.56	-45.6	132	1.581	471.7	0.377	0.382	0.35±.05
					500	0.356	0.314	
					490	0.363		
					503	0.354		
				1.590				
					448(30°)			
					488(30°)			
o-Dichlorobenzene	147.01	-17.0	180.5	0.196	145.2	0.198	0.193	0.19±.01
					145	0.198		
					152	0.190		
					92.7			
				0.20				
m-Dichlorobenzene	147.01	-24.7	173	0.307	123.2	0.366		0.36±.02
					123	0.366		
					120	0.367		
p-Dichlorobenzene	147.01	53.1	174	0.0902[c]	83.1	0.160	0.240	0.16±.02
					87.2	0.152		

(continued)

[a] Extrapolated values from liquid state.

[b] Calculated from the extrapolated vapor pressure with a fugacity ratio correction.

[c] Extrapolated from solid vapor pressure.

[d] Calculated using atmospheric pressure.

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa*	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
					79 76 90.6	0.168 0.174 0.146		
1,2,3-Tri-chlorobenzene	181.45	53	218	0.0530^a 0.0280^b	16.6 31.5	0.306 0.161	0.127	
1,2,4-Tri-chlorobenzene	181.45	16.95	213.5	0.0606	25.03 34.57	0.439 0.318		
1,3,5-Tri-chlorobenzene	181.45	63	208	0.077^a	25.03 6.59	0.233 0.0884		
1,2,3,4-Tetra-chlorobenzene	215.9	47.5	254	0.00876^a 0.00521^b	4.31	0.261		
1,2,3,5-Tetra-chlorobenzene	215.9	54.5	246	0.0186^a 0.0098^b	3.50	0.593	0.159	
1,2,4,5-Tetra-chlorobenzene	215.9	140	243	0.0101^a 0.00072^b	0.595	0.261		
Pentachloro-benzene	250.3	86	277	8.89×10^{-3a} 2.19×10^{-3b}	0.560	0.977		
Hexachloro-benzene	284.8	230	322	3.44×10^{-4a} 1.45×10^{-6} (20°)	0.0050	0.0050 (20°)		

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol[a]		
						calc	exptl	recom
2-Chloro-toluene	126.6	-39	179.3	0.173 0.236(20°)	466 (30°)	0.0641 (30°)		
Fluorobenzene	96.11	-41.2	85.1	10.20	1553 1540 (30°)	0.631		0.63±.06
a,a,a-Tri-fluorotoluene	146.11	-29.11	102.06	4.98	450.7	1.61		
Bromobenzene	157.02	-30.82	156	0.552	410 360	0.211 0.241	0.247	0.21±.04
				0.570				
					500 (20°) 446 (30°)			
				0.997(35°)	458 (35°)	0.342 (35°)		
m-Dibromo-benzene	235.92	-7	218	0.057(35°)	67.47 (35°)	0.199 (35°)		
p-Dibromo-benzene	235.92	87.33	219	0.0215 0.018(35°)	20.0 26.42 (35°)	0.254 0.161 (35°)		
2-Bromoethyl-benzene	185.07	-67.5	218	0.0326[a]	39.05			

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure P, kPa *	Solubility S, g/m^3	Henry's law constant kPa m^3/mol[a] calc	exptl	recom
Iodobenzene	204.01	-31.21	188.3	0.132	180 229 340 (30°)	0.150 0.118		0.13±.02
p-Diiodobenzene	329.91	131	285		1.4 1.86			
1,4-Bromo-chlorobenzene	191.46	68	196	0.0344	44.88	0.147		
1-Chloro-naphthalene	162.62	-2.3	258.8		22.4		0.355	
2-Chloro-naphthalene	162.62	61	256		11.7		0.0319	

[a] Extrapolated from liquid state.

[b] Calculated from the extrapolated vapor pressure with a fugacity ratio correction.

[c] Extrapolated from solid vapor pressure.

Data for pesticides

Lindane	290.83	112.9		8.39×10^{-6} 4.35×10^{-6} (20°) 4.13×10^{-6} (20°) 2.80×10^{-6} (20°)	7.3 7.80	3.34×10^{-4} 3.13×10^{-4}		$(3.2 \pm .2) \times 10^{-4}$

(continued)

TABLE 2.2 (continued)

Compound	MW	mp,°C	bp,°C	Vapor pressure p, kPa*	Solubility S,g/m^3	Henry's law constant kPa m^3/mol^a calc	exptl	recom
				(20°)				
				1.25×10^{-6}				
				(20°)				
				4.0×10^{-3}				
				(20°)				
Aldrin	357.9	59.60		7.99×10^{-7}	0.2	1.43×10^{-3}		$(2.8\pm1.4)\times10^{-3}$
					0.017	4.09×10^{-3}		
Dieldrin	373.9	175		6.59×10^{-7}	0.25	9.86×10^{-4}		$(1.1\pm.2)\times10^{-3}$
					0.20	1.23×10^{-3}		
				3.47×10^{-7}				
				(20°)				
				3.87×10^{-7}				
				(20°)				
				2.53×10^{-7}				
				(20°)				
				1.04×10^{-7}				
				(20°)				
				2.67×10^{-8}				
				(20°)				
				2.37×10^{-8}				
				(20°)				
DDT	354.5	109	185	1.34×10^{-8}	1.2×10^{-3}	3.9×10^{-3}		$(5.3\pm3.8)\times10^{-3}$
					(20°)	(20°)		
					5.5×10^{-3}	8.46×10^{-3}		
					(20°)	(20°)		
					3.1×10^{-3}	1.53×10^{-3}		
					(20°)	(20°)		
				2.53×10^{-8}	1.0×10^{-3}	8.97×10^{-3}		
				(20°)				

(continued)

TABLE 2.2 (continued)

Compound	MW	mp, °C	bp, °C	Vapor pressure p, kPa*	Solubility S, g/m^3	Henry's law constant kPa m^3/mol^a		
						calc	exptl	recom
Parathion	297.27	6.1 (76)	113/ .0067 (76)	5.04×10^{-6} (20°)	24 11.9(20°)	1.23×10^{-4}		
					11.0(40°)			
				2.61×10^{-6} (20°) 5.85×10^{-7} (20°) 7.6×10^{-7} (20°)				
Methyl-parathion	263.18	35-36 (76)	109/ .0067 (76)	3.94×10^{-6} (20°)	25(20°)	$4.51\times1-^{-5}$		$(2.0\pm1.0)\times10^{-5}$
					77(40°)			
				1.29×10^{-6} (20°)				
Malathion	330.36	2.85 (99)	120/ .027 (76)	1.67×10^{-5} (20°)	145(20°)	3.80×10^{-5}		
				7.33×10^{-7} (30°)				
Chlor-phrifos	350.58	41.5-43 (76,102,103,104)		2.49×10^{-6}	0.4(23°)			
				2.53×10^{-6}				

* 100 kPa=100,000 Pascals (Pa)= 14.50 pounds per square inch=750 mm Hg(0°c)= 1 bar= .987 atmospheres.

[a] calculated using atmospheric pressure.

For appropriate references see Mackay and Shiu (1981).

water in the porous medium. Compounds with high water solubility (from surface spills) would of course have shorter downward travel times as reflected by classical breakthrough curve analysis. Pfannkuch (1984) points out that for oil spills the hydrocarbon components with differing solubilities will dissolve out differentially and will produce a simultaneous ageing and leaching effect on the spill. See tables by Mackay and Shiu (1981) for a listing of the solubilities of various organic compounds.

(3) Henry's law constant (K_H): According to Mackay and Shiu (1981), "The Henry's law constant is conventionally expressed as a ratio of partial pressure in the vapor to the concentration in the liquid." It is thus a coefficient that reflects the air-water partitioning. Such information is helpful in understanding in what phase an organic compound would most likely be found. Thus, an organic compound with a high vapor pressure and low water solubility would be expected to be favored in the vapor phase and would therefore be a relatively good candidate for soil vapor monitoring. However, if the detection of organics in ground water is of primary interest, a false positive might result from this situation. The relationship between solubility and vapor pressure is plotted in Figure 2.1 by Mackay and Shiu (1981) and shows that compounds within a homologous series generally lie on a 45° diagonal of constant Henry's law constant and that pesticides typically have very low vapor pressures. Marin and Thompson (1984) have found that actual field partition coefficients are less than laboratory coefficients and that the field data suggest larger partitioning into the liquid (ground water) phase. They theorize that this is probably the result of either lateral diffusion or ofequilibrium conditions that are typically never achieved in the field between diffusion in soil gas and water.

(4) Concentration: The concentration refers to the amount of organic compound per unit amount of solvent (air/water) in units such as g/m^3, ppb/v. Kreamer (1982) concluded that the diffusion of a gas from areas of high concentration to low, resulting only from the existing concentration gradient, was the mechanism of greatest importance for gas transport in the unsaturated zone. The concentration of the organic compound in the ground

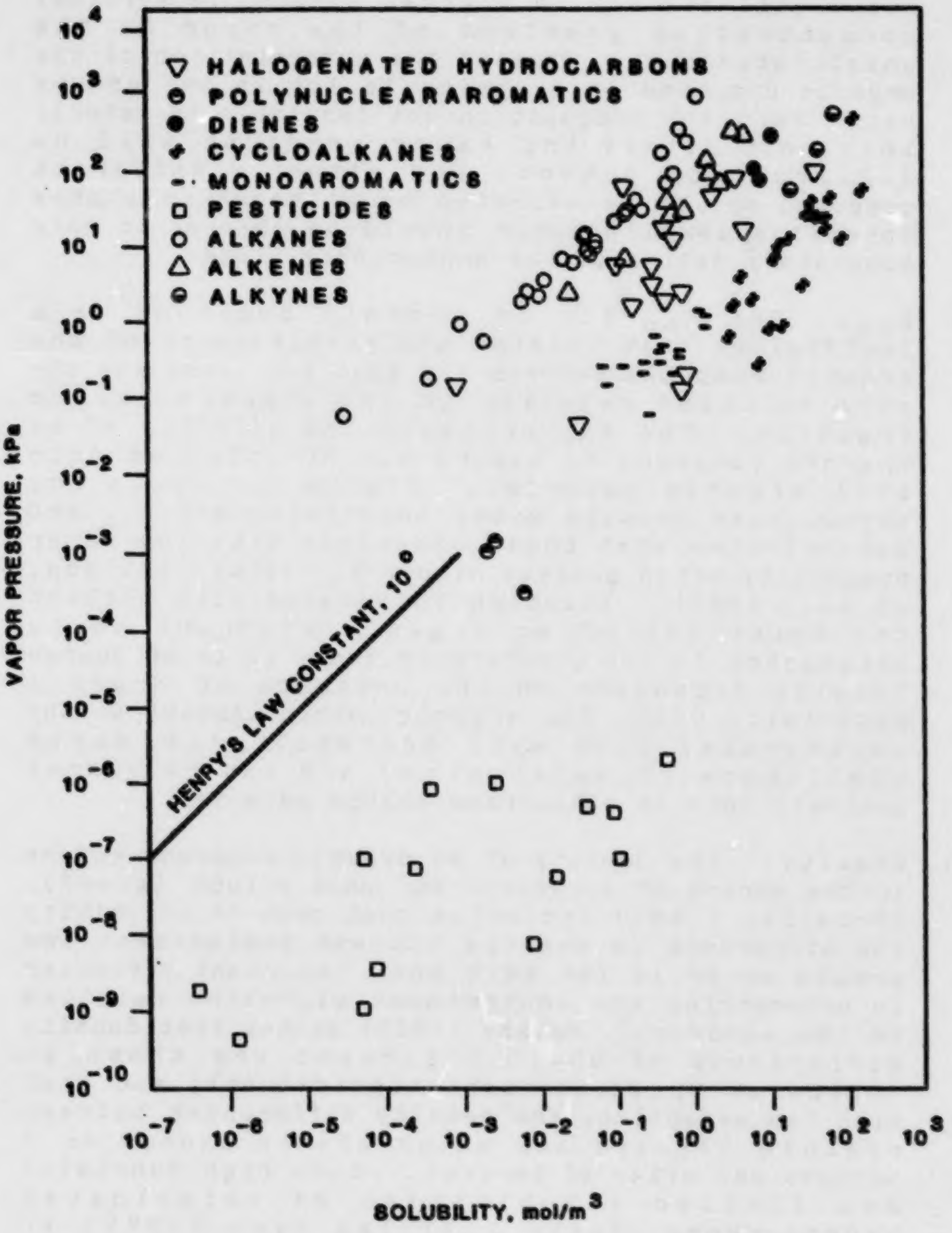


Figure 2.1. Plot of solubility vs vapor pressure illustrating the tendency for compounds in a homologous series to lie on a 45° diagonal of constant Henry's law constant (MacKay and Shiu, 1981).

water will dictate to a great extent the vertical concentration gradient of the vapor in the unsaturated zone. Thus if the concentration of the organic compound in question is low in the ground water (and the compound is not insoluble in water), then most likely the vapor gradient will be difficult to detect, and either a different compound should be selected as a tracer or a more intensive sampling grid should be imposed to more accurately delineate the contaminant plume.

(5) K_{oc}: The K_{oc} for an organic compound is a coefficient that relates the partitioning of the organic compound between the adsorbed phase and the soil solution relative to the organic carbon fraction. The K_{oc} reflects the affinity of an organic compound to adsorb out of solution onto soil organic material. Figure 2.2 shows the correlation between water solubility and K_{oc} and demonstrates that those compounds with low water solubility often possess higher K_{oc} values (Wilson, et al., 1981). Although this value will reflect the potential of an organic compound to be attenuated in the unsaturated zone, it is of course totally dependent on the presence of organic material. Often the organic carbon content in the unsaturated zone will decrease with depth (influence of vegetation) and can be almost entirely void in subsurface coarse material.

(6) Density: The density of an organic compound refers to the amount of substance per unit volume (g/cm^3). [Schwille (1984) indicates that next to solubility the difference in density between contaminant and ground water is the next most important parameter in determining the contaminant migration relative to the aquifer.] Mackay (1985) states that density differences of about 1 percent are known to influence fluid movement significantly and that with few exceptions the density differences between organic liquids and water are in excess of 1 percent and often 10 percent. Such high densities and limited solubilities of chlorinated hydrocarbons (Table 2.3) led Byer (1981) to conclude that this was the primary cause for the widespread chlorinated hydrocarbon contamination of underground water sources. Byer (1981) also showed how the density of an organic compound such as TCE can be used effectively to trap the compound in a recovery process (Figure 2.3).

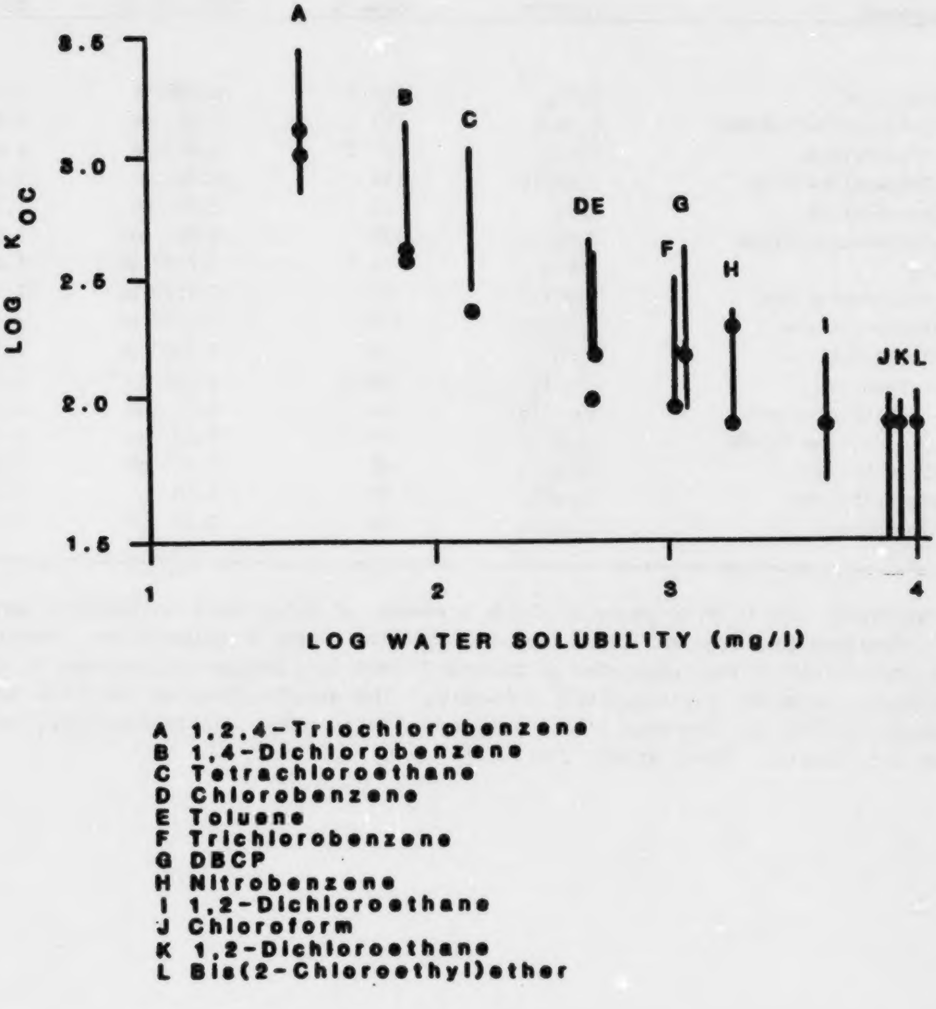


Figure 2.2. Relationship between the water solubility of a compound (mg/liter) and its partition coefficient between soil organic C and soil solution (K_{OC}) (Wilson, et al., 1981).

TABLE 2.3 CHLORINATED HYDROCARBONS

Compound	Chemical Formula	B P oC 760mm Hg.	Solubility in 100g H_2O (1)	Density 20/4°C
Hexachloroethane	C_2Cl_6	186.3	0.005 gm	2.2091
1,1,1,2,2-Pentachloroethane	C_2HCl_5	162	0.05 gm	1.6796
Tetrachloroethylene	C_2Cl_4	121.2	0.015 gm	1.6227
1,1,2,2-Tetrachlorethane	$C_2H_2Cl_4$	146	0.29 gm	1.5953
Carbontetrachloride	CCl_4	76.7	0.08 gm	1.5940
1,1,1,2-Tetrachloroethane	$C_2H_2Cl_4$	129	0.015 gm	1.59069
Chloroform	$CHCl_3$	61.7	0.8220 gm	1.4832
1,2,2-Trichloroethylene	C_2HCl_3	87	0.1100 gm	1.4642
1,1,2-Trichloroethane	$C_2H_3Cl_3$	113.5	0.4500 gm	1.4397
1,1,1-Trichloroethane	$C_2H_3Cl_3$	74	0.4400 gm	1.3390
Methylene Chloride	CH_2Cl_2	40.4	2.000 gm	1.3266
Cis-1,2-Dichloroethylene	$C_2H_2Cl_2$	60	0.35 gm	1.2837
Trans 1,2-Dichloroethylene	$C_2H_2Cl_2$	47	0.63 gm	1.2565
1,2-Dichloroethane	$C_2H_4Cl_2$	83	0.869 gm	1.2351
1,1-Dichloroethylene	$C_2H_2Cl_2$	37	4.00 gm	1.218
1,1-Dichloroethane	$C_2H_4Cl_2$	57	0.55 gm	1.1757

[1] Chlorination of simple hydrocarbons yields a variety of chlorinated hydrocarbons varying in physical properties in a regular fashion depending upon the degree of chlorination. Usually, as the chlorine content of the hydrocarbon is increased there is a progressive decrease in specific heat, dielectric constant and solubility in water. The substitution of chlorine onto the hydrocarbon imparts an increase in solvent power, viscosity, nonflammability, chemical reactivity and density. (Byer, et al., 1981)

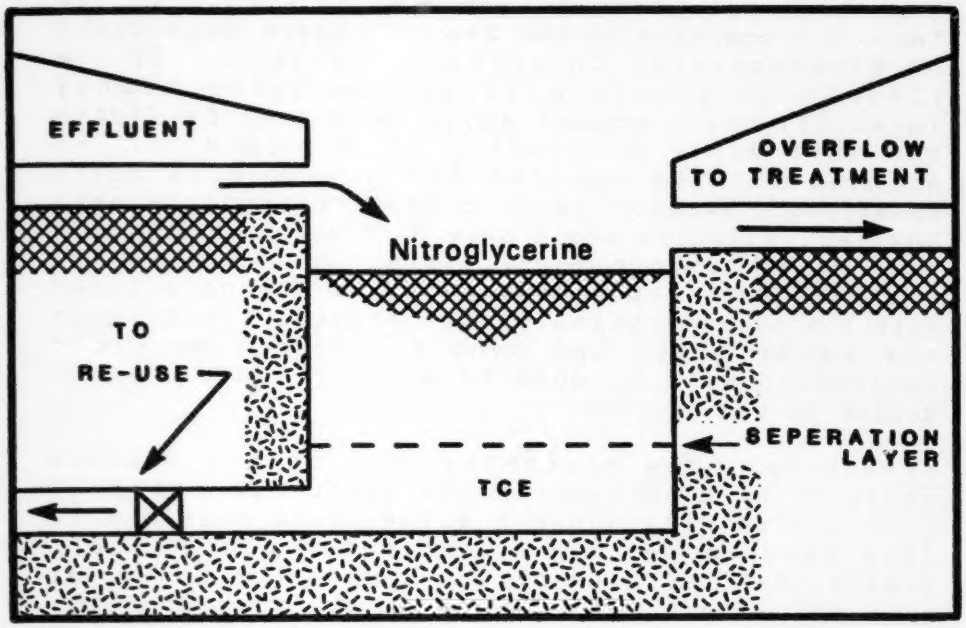

EFFLUENT
OVERFLOW TO TREATMENT
Nitroglycerine
TO RE-USE
SEPERATION LAYER
TCE

Figure 2.3. Diagram showing an economical and safe way to contain a chlorinated hydrocarbon (TCE) compound. The so-called nitroglycerine trap collects TCEs from the plant via floor drains. Traps must be concrete lined to prevent seepage. It is economical to reprocess TCE when volume used is large (Byer, 1981).

Organic compounds with specific gravities of less than 1.0 associated with solubilities of less than 1 percent are often referred to as floaters, see Table 2.4 compiled by the New York State Department of Environmental Conservation (1983). If the floater is also classified as being highly volatile, the compound would be a good candidate for soil vapor monitoring as it would not be diluted in the aquifer and potentially could establish a steeper vapor concentration gradient. However, floaters would have difficulty moving past subsurface obstructions. Thus, it would also be critical that vapor concentrations be correlated with the concentration of the organic floating at the water table and that a properly screened monitoring well be used to avoid sampling water deeper in the aquifer.

(7) Viscosity: The viscosity of a liquid organic compound is a measure of the degree to which it will resist flow under a given force measured in dyne-seconds per cm^2. According to Schwille (1984),the viscosity of the organic fluid (such as oil) will affect the velocity of the flow process. Mackay (1985) adds that it is the combination of density and viscosity that will govern the migration of an immiscible organic liquid in the subsurface. Thus, it is the viscosity of an immiscible organic fluid (such as oil) that will control the lens thickness on a water table. However, even with high viscosity fluids such as oils, Holzer (1976) points out that many months after a spill, it is often too late to determine whether the spill was caused by a catastrophic release or a slow steady "drip". Figure 2.4 shows that after 300 days, little difference is noted in the thickness of a spill developed under two different permeability values.

(8) Dielectric constant: The dielectric constant of a medium is a parameter that relates the relationship between two charges and the distance of separation of the two charges to the force of attraction. In a clay medium this constant reflects the degree to which the clays will either shrink or swell. Liquids with a high dielectric constant (Table 2.5) such as water would be expected to cause the clays to swell. Conversely, those liquids with a low dieletric constant would cause the clays to shrink and, therefore, increase in permeability after exposure to concentrated organic liquids. Table

TABLE 2.4. LIQUID GROUP CLASSIFICATION OF VARIOUS ORGANIC COMPOUNDS

Liquid	Poisonous	Flammable	Corrosive	Reactive	Volatile	Floater	Amenable to biological treatment	Bio-degradeable	Highly toxic to aquatic life
Acetaldehyde	–	x	–	–	x	–	x	x	–
Acetic acid	–	–	x	–	–	–	x	x	–
Acetic anhydride	–	–	x	x	–	–	x	x	–
Acetone cyanohydrin	x	–	–	–	–	–	x	x	–
Acetyl bromide	–	–	x	x	–	–	x	x	x
Acetyl chloride	–	x	–	x	x	–	x	x	–
Acrolein	x	x	–	x	x	–	x	x	x
Acrylonitrile	–	x	–	–	x	–	x	x	–
Allyl alcohol	x	x	–	–	x	–	x	x	–
Allyl chloride	x	x	–	–	x	x	x	x	–
Ammonium hydroxide	–	–	x	–	–	–	x	–	–
Amyl acetate	–	x	–	–	–	x	x	x	–
Aniline	x	–	–	–	–	–	x	x	–
Benzene	–	x	–	–	x	x	x	x	–
Benzonitrile	–	–	–	–	–	–	x	x	–
Benzoyl chloride	–	–	x	x	–	–	x	x	–
Benzyl chloride	–	–	x	–	–	–	x	x	–
Bis(chloromethyl) ether	x	–	–	–	x	–	x	x	ND
Bis (2-chloroisopropyl) ether	–	–	–	–	x	–	x[b]	x[b]	ND
Bis (2-chloroethoxy) methane	–[b]	–[b]	–[b]	–[b]	x[b]	–[b]	x	x	ND
Bis (2-chloroethyl) ether	x	–	–	–	x	–	x	x	ND
Bis (2-ethylhexy) phthalate	x	–	–	–	x	x	–	–	ND
Bromoform (tribromomethane)	–	–	–	–	–	–	–	–	ND
Butyl acetate	–	x	–	–	–	x	x	x	–
Butylamine	–	x	–	–	x	–	x	x	–
Butyl benzyl phthalate	–	–	–	–	–	–	x	x	–
Butyric acid	–	–	x	–	–	–	x	x	–

(continued)

TABLE 2.4.(continued)

Liquid	Poisonous	Flammable	Corrosive	Reactive	Volatile	Floater	Amenable to biological treatment	Bio-degradeable	Highly toxic to aquatic life
Carbon disulfide	-	x	-	-	x	-	-	-	-
Carbon tetrachloride	-	-	-	-	x	-	-	-	-
Chlordane	-	-	-	-	-	-	-	-	x
Chlorobenzene	-	x	-	-	-	-	x	x	-
Chlorodibromomethane	-	-	-	-	x	-	-	-	ND
Chloroethane	x	x	-	-	x	x	x	x	ND
2-Chloroethyl vinyl ether	-	x	-	-	x	-	x	x	ND
Chloroform	-	-	-	-	x	-	x	-	ND
2-Chlorophenol	x	-	-	-	-	-	x	x	-
4-Chlorophenyl phenyl ether	x[b]	-[b]	-[b]	-[b]	x[b]	-[b]	-	-	-
Chlorosulfonic acid	-	-	x	x	-	-	x	x	ND
Crotonaldehyde	x	x	x	-	x	x	x	x	-
Cyclohexane	-	x	-	-	x	x	x	x	x
Diazinon	-	-	-	-	-	-	-	-	ND
1,2-Dichlorobenzene	-	-	-	-	-	-	x	x	-
1,3-Dichlorobenzene	-	-	-	-	-	-	x	x	-
Dichlorobromomethane	-[b]	-[b]	-[b]	-[b]	-[b]	-	-	-	ND
1,1-Dichloroethane	-	x	-	-	x	-	x	x	ND
1,2-Dichloroethane	-	x	-	-	x	-	x	x	-
1,1-Dichloroethylene (vinylidene chloride)	-	x	-	-	x	-	-	-	ND
1,2-Dichloropropane	-	x	-	-	x	-	x	x	-
2.2-Dichloropropionic acid	-	-	x	-	-	-	-	-	
1,3-Dichloropropylene	x	x	-	-	x	-	x	x	-
Dichlorovos	-	-	x	-	-	-	-	-	x
Diethylamine	-	x	x	-	x	x	x	x	ND
Diethyl phthalate	-	-	-	-	x	-	x	x	ND
Dimethyl phthalate	-	-	-	-	x	-	x	x	ND
Di-n-octyl phthalate	x	-	-	-	x	-	x	x	ND

(continued)

TABLE 2.4(continued)

Liquid	Poisonous	Flammable	Corrosive	Reactive	Volatile	Floater	Amenable to biological treatment	Bio-degradeable	Highly toxic to aquatic life
Di-n-octyl phthalate	-	-	-	-	x	-	x	x	ND
Disulfoton	x	-	-	-	-	-	-	-	ND
Dodecylbenzenesulfonic acid	-	-	x	-	-	-	x	x	ND
Endrin aldehyde	-	-	-	-	-	-	_b	_b	x
Epichlorohydrin	x	x	x	-	-	-	x	x	-
Ethion	-	-	-	-	-	-	-	-	x
Ethylbenzene	-	x	-	-	x	x	x	x	-
Ethylene dibromide	x	-	x	-	x	-	x	x	-
Ethylenediamine	-	x	-	-	-	-	x	x	-
Formic acid	-	-	x	-	-	-	x	x	-
Furfural	-	-	x	-	-	-	x	x	-
Hexachlorobutadiene	-	-	-	-	-	-	x	-	ND
Hydrochloric acid	-	-	x	-	-	-	x	-	-
Hydrofluoric acid	-	-	x	-	-	-	x	-	-
Isophorone	-	-	-	-	-	x	x	x	ND
Isoprene	-	x	-	-	x	x	x	x	-
Malathion	-	-	-	-	-	-	-	-	x
Methylene chloride (dichloromethane)	-	-	-	-	x	-	-	-	ND
Methyl methacrylate	-	x	-	-	x	x	x	x	-
Mevinphos	x	-	x	-	-	-	-	-	x
Naphthenic acid	-	-	x	-	-	-	x	x	-
Nitric acid	-	-	x	-	-	-	x	-	-
Nitrobenzene	x	-	-	-	-	-	x	x	-
N-nitrosodimethylamine	-	-	-	-	x	-	-	-	ND
N-nitrosodi-n-propylamine	_b	_b	_b	_b	x^b	_b	-	-	ND
Parathion	x	-	-	-	-	-	x	x	x
Phosphorous oxychloride	-	-	x	x	-	-	x	x	-
Phosphorous trichloride	-	-	x	x	x	-	x	-	-
Polychlorinated biphenyls (PCBS)	-	-	-	-	-	-	-	-	x
Propionic acid	-	-	x	-	-	-	x	x	-

(continued)

TABLE 2.4.(continued)

Liquid	Poisonous	Flammable	Corrosive	Reactive	Volatile	Floater	Amenable to biological treatment	Bio-degradeable	Highly toxic to aquatic life
Propionic anhydride	-	-	x	x	-	-	x	x	-
Propylene oxide	-	x	-	-	x	-	x	x	ND
Quinoline	-	-	-	-	-	-	-	-	-
Styrene	-	x	-	-	x	x	x	x	-
Sulfuric acid	-	-	x	-	-	-	x	-	-
Sulfur monochloride	-	-	x	x	-	-	x	-	-
2,4,5-Trichlorophenoxy acetic acid with amines	-	x	-	-	x	-	-	-	-
1,1,2,-Tetrachloroethane	-	-	x	x	x	-	-	-	ND
Tetrachloroethylene	-	-	-	-	x	-	-	-	ND
Tetraethyl pyrophosphate	x	-	-	x	-	-	-	-	ND
Toluene	-	x	-	-	x	x	x	x	-
1,2-trans-Dichloroethylene	-	-	-	-	x	-	x	x	ND
1,2,4-Trichlorobenzene	-	-	-	-	-	-	x	x	ND
1,1,1-Trichloroethane	-	-	-	-	x	-	x	x	ND
1,1,2-Trichloroethane	-	-	-	-	x	-	x	x	-
Trichloroethylene	-	-	-	-	x		x	x	ND
Triethylamine	-	x	x	-	x	x	x	x	-
Vinyl acetate	-	x	-	-	-	x	x	x	-
Vinyl chloride (chloroethylene)^b	-	x	-	-	x	x	x	x	ND
Xylene	-	x	-	-	-	x	x	x	-

x Denotes chemical is in this category.
- Denotes chemical is not in this category.
ND Denotes no data available.
b Denotes assumed values based on chemical groups of similar type substances.

(New York State Department of Environmental Conservation, 1983)

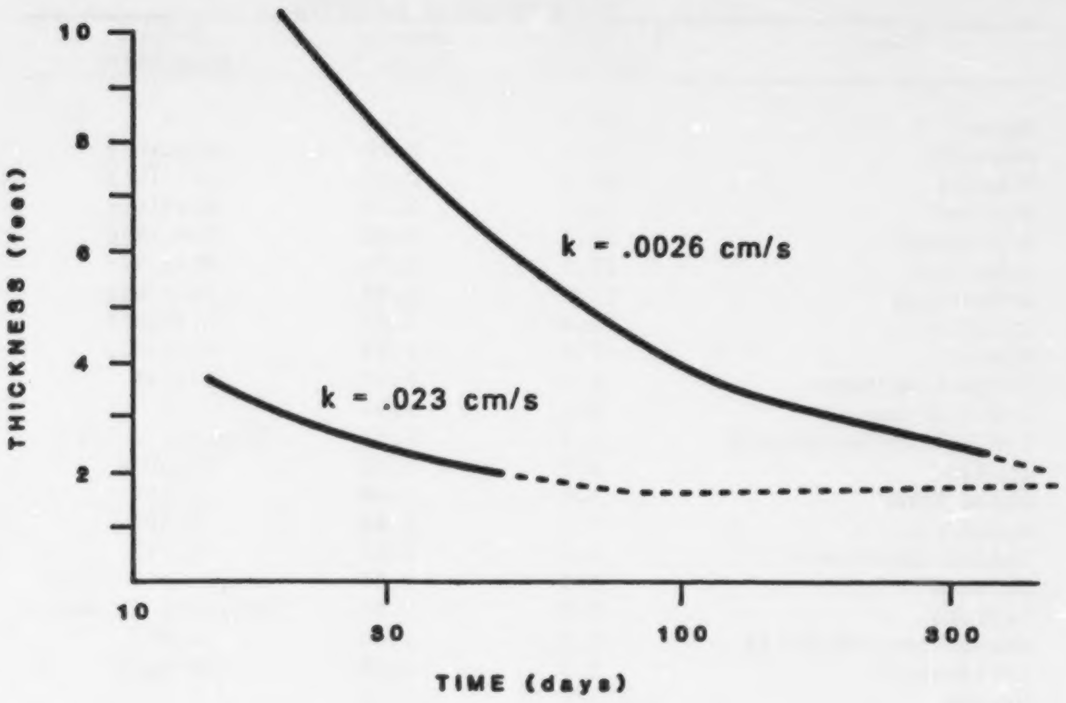


Figure 2.4. Thickness of center of oil lens versus time where k values are permeabilities with respect to oil (Holzer, 1976).

TABLE 2.5. DIELECTRIC CONSTANTS, DENSITIES AND WATER SOLUBILITIES OF VARIOUS HALOGENATED AND NONHALOGENATED SOLVENTS

Name	Dielectric Constant	Density (g/cm^3)	Water Solubility
Water	78.5	1.00	-
Methanol	32.7	0.79	Miscible
Ethanol	24.6	0.79	Miscible
Acetone	20.7	0.79	Miscible
1-Propanol	20.3	0.80	Miscible
1-Butanol	17.5	0.81	Miscible
b-Pentanol	13.5	0.81	Miscible
Pyridine	12.4	0.97	Miscible
Phenol	9.8	1.05	Miscible
Dichloromethane	8.9	1.31	1.32%
1-Bromopropane	8.1	1.34	-
1,1,1-Trichloroethane	7.5	1.34	Slightly Soluble
Aniline	6.9	1.02	Soluble
Chloroform	4.8	1.48	0.82%
Bromoform	4.4	2.89	0.10%
Trichloroethylene	3.4	1.48	0.11%
Toluene	2.4	0.87	Slightly Soluble
Benzene	2.3	0.88	Slightly Soluble
Carbon tetrachloride	2.2	1.60	0.08%
Cyclohexene	2.0	0.78	40 mg/l
Hexane	1.9	0.65	-
Tetrachloroethylene	2.2	1.6	150 mg/l

(Anderson, et al., 1984)

TABLE 2.6 INTRINSIC PERMEABILITY OF SOILS PERMEATED BY WATER AND ORGANIC LIQUIDS

	Intrinsic Permeability ($10^{-9}cm^2$)				
	Nonpolar Solvents		Polar Solvents		
Soil type	Water	Kerosene	Xylene	Ethylene glycol	Isopropyl alcohol
Sand	145.	179.	151.	135.	177.
Sandy-clay	1.6	158.	146.	62.8	93.2
Clay	0.5	10.1	14.0	2.4	6.4

(Anderson, et al., 1984)

2.6 (Anderson, et al., 1984) shows the impact various solvents will have on the intrinsic permeability of various soil types. Such a result would of course mean that in a clay soil or horizon the concentrated organic plume will reach the ground water in a shorter travel time and that the plume would expand to a larger volume. In addition, the vapor phase moving back toward the surface in the same area would not be restricted to the same degree.

(9) Boiling Point: The boiling point of a compound is the temperature at which the external pressure of the liquid is in equilibrium with the saturation vapor pressure of the liquid. Thus, for higher boiling points there is a general association with lower vapor pressures. Again, it is those organics with higher vapor pressures and thus lower boiling points that would be better suited for soil vapor monitoring. A listing of the boiling points for various organic compounds is included in table 2.2 compiled by Mackay and Shiu (1981).

(10) Molecular weight: The molecular weight of an organic compound is the sum total of the weights of the atoms that compose it (see table 2.2). Mackay and Shiu (1981) indicate that for liquid alkanes there is a tendency for the Henry's law constant to increase with increasing molecular weight as the solubility falls more than the vapor pressure. High molecular weight hydrocarbons (especially aromatics) are decomposed through biodegradation at a much slower rate (American Petroleum Institute, 1972) and thus would persist in the unsaturated and saturated zones longer.

PROPERTIES OF THE UNSATURATED ZONE

(1) Air filled porosity: The air filled porosity of a porous medium, such as soil is defined as the ratio of the volume of air in the soil pores to the total volume (volume of air, water, and soil combined). It is thus indicative of soil aeration and is inversely related to the degree of saturation. The air-filled porosity is an important parameter in estimating the diffusion of gas in soil and unconsolidated material. The diffusion coefficient of oxygen is approximately 10,000 times lower in water than in air (Letey, et al., 1964). Thus, soil organic vapors migrating toward the soil surface would be restricted if the water content

increases and the air-filled porosity decreases. Vapors moving into low air-filled porosity zones could potentially be resolubilized. Because of the restrictions in flow and the possible resolubilization, vertical soil gas profiles would be poorly established. This parameter would be expected to change dramatically in the unsaturated zone as it is dependent on the position relative to a wetting front (rainfall) and on changes in texture (water holding capacity).

(2) Volumetric water content: The volumetric water content is the ratio of the volume of water in a porous medium to the total volume. When the water fills the entire pore volume the medium is saturated. Coarse soils have lower volumetric water contents at saturation than do medium textured soils and medium textured soils less than clayey soils. Under unsaturated flow conditions, it is the unsaturated hydraulic conductivity and the hydraulic head gradient that dictate the change in volumetric water content with time. As the volumetric water content increases, the air filled porosity decreases, and the path for vapor flow becomes restricted. Thus, as the percent water in the soil pores goes up, the possibility of a vertical soil organic vapor gradient being established is lessened and so is the likelihood of correlating soil gas measurements with ground water concentrations. Reid (1985) has indicated little success in soil vapor monitoring studies when the vadose zone contains high clay and water contents. Water content in subsurface layers has also been shown to be the decisive factor in determining the shape of an oil body and the distribution after percolation (Scwille, 1975).

(3) Soil organic matter: The amount of organic matter in a soil varies according to the vegetation, climate, and the rate of decomposition. Agricultural soils often possess in excess of 2 percent organic matter whereas desert soils can be almost entirely void of organic matter. Organic material generally has high surface areas and exchange properties ideal for adsorption of organic compounds. The K_{OC} value reflects the impact of this organic material to adsorb organic compounds out of solution. Chiou (1985) states that "the extent of uptake of nonionic organic compounds from water on a great variety of soils is closely related to soil organic matter content." Chiou

also indicates that "when soils are fully hydrated, adsorption of the organic solutes by soil minerals becomes relatively insignificant compared to the uptake by partitioning into soil organic matter, presumably because water is preferentially adsorbed by minerals."

(4) Soil texture: The texture of a soil refers to the proportions of various particle size groups in a soil mass. These particle size groups are typically called sand, silt, and clay. Figure 2.5 shows the textural triangle and the various soil textural classes. As the clay content increases, the water holding capacity increases, the exchange capacity increases, and the rate of diffusion decreases. Thus, if a high clay content layer exists in the subsurface (textural discontinuity) or if the entire vadose zone is comprised of clayey soil, it will act as a retarding layer to the vertical flux of volatile organic carbons. Swallow and Gschwend (1983) point out that it is the rate of flux through the most retarding layer that will control the vertical flux. Figure 2.6 (American Petrolem Institute, 1972) shows the possible effects of clay layers and lenses on the migration of contaminants in the unsaturated zone. Indurated layers such as petro calcic layers can also alter the flow path of contaminants both in the liquid and vapor phases. Conversely, gravel layers have been shown to act as a conduit for organic vapors to diffuse laterally from more contaminated soils (Marin, et al., 1984).

(5) Vapor pressure of water in the soil pores: The aqueous vapor pressure measured in soil pores is for the most part considered to be vapor saturated: as Hillel (1971) points out, a change in matric suction between 0 and 100 bars is accompanied by a vapor pressure change of only 1.6 millibars. Temperature has a much larger impact on vapor pressure as a $1^{\circ}C$ change has almost the same effect as the 100-bar suction change. Since vapors tend to move from warm to cold areas in a soil, the vapors would therefore tend to move downward during the day and upward during the night. At the soil surface and perhaps down even several inches, the vapor pressure can drop below saturation because of higher gas mixing and exchange rates. The presence of electrolytes (often concentrated near the soil surface via evaporation) can also lower the vapor pressure. If the vapor pressure in the soil pores

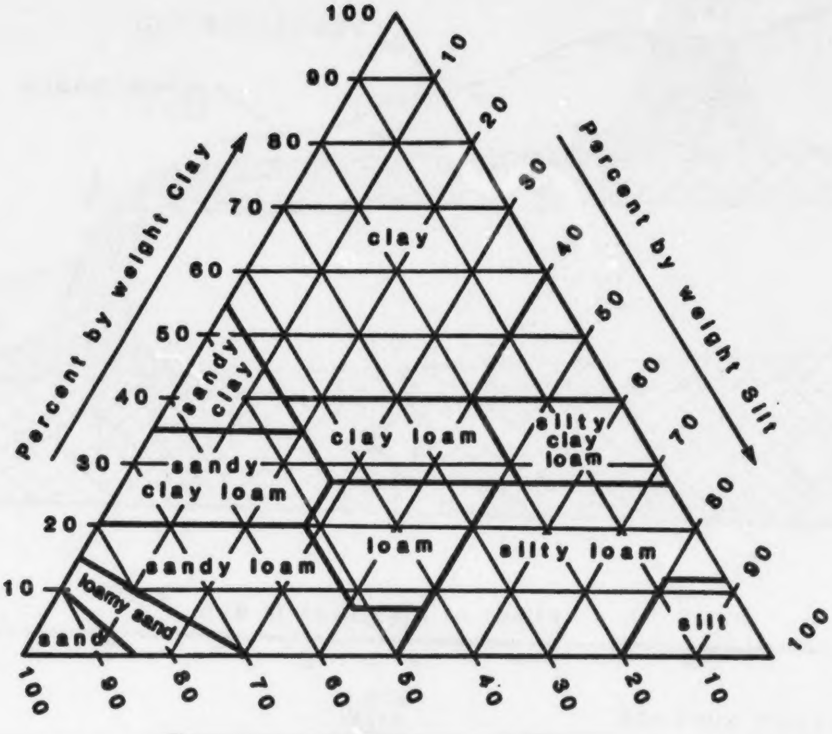
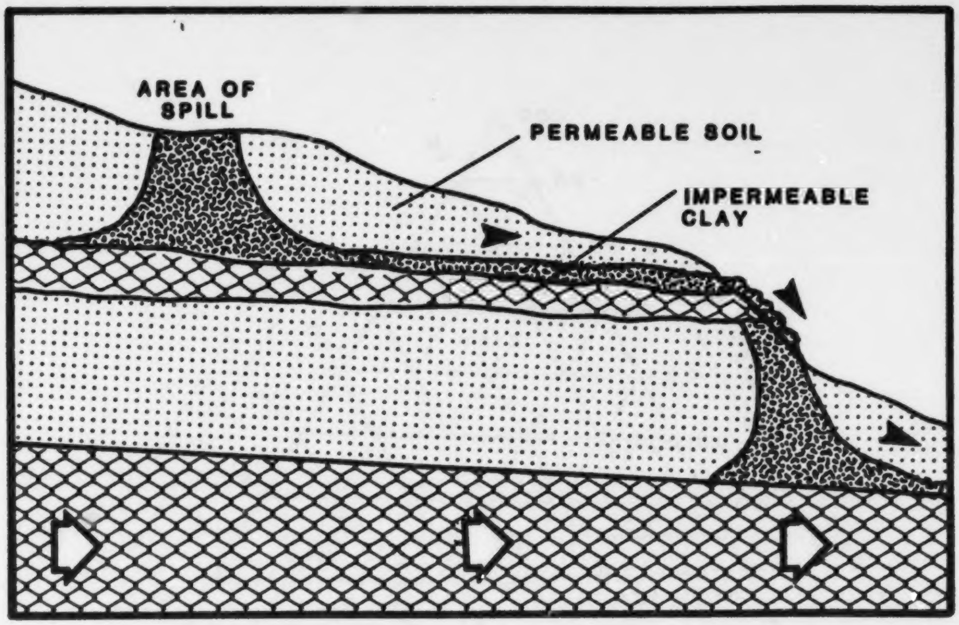

100
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
100
Percent by weight Clay
Percent by weight Silt
clay
sandy clay
clay loam
silty clay loam
sandy clay loam
loam
silty loam
sandy loam
loamy sand
sand
silt
100
90
80
70
60
50
40
30
20
10
Percent by weight Sand

Figure 2.5. Textural triangle, showing the percentages of clay (below 0.002 mm), silt (0.002-0.05 mm), and sand (0.05-2.0 mm) in the basic soil textural classes (American Petroleum Institute, 1972) (Hillel, 1971).

Possible Migration of Product to Outcrop
Followed by Second Cycle Contamination


AREA OF SPILL
PERMEABLE SOIL
IMPERMEABLE CLAY

Effect of Clay Lens in Soil

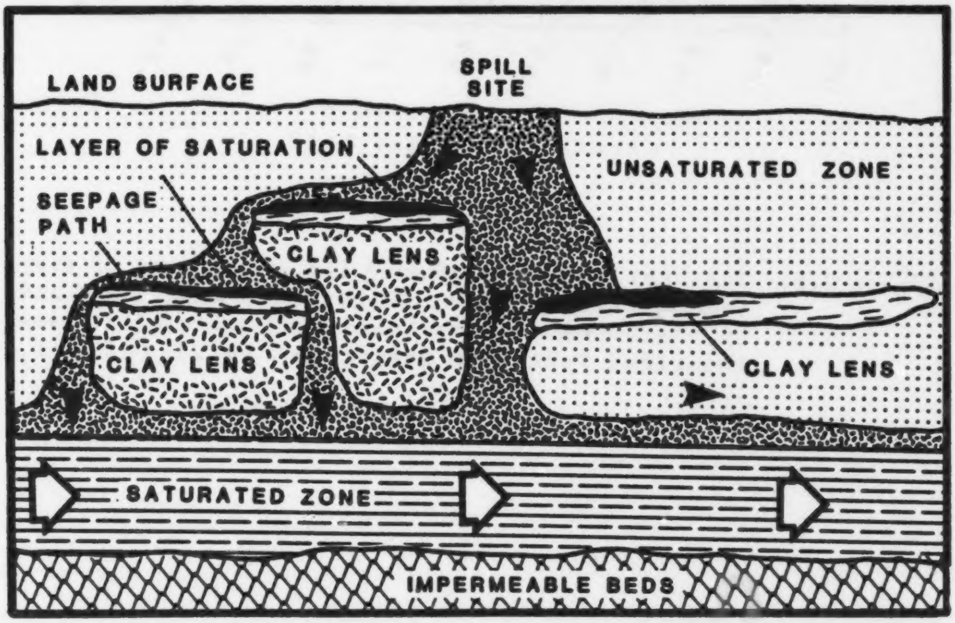

LAND SURFACE
SPILL SITE
LAYER OF SATURATION
UNSATURATED ZONE
SEEPAGE PATH
CLAY LENS
CLAY LENS
CLAY LENS
SATURATED ZONE
IMPERMEABLE BEDS

Figure 2.6. Possible migration of product to outcrop followed by second cycle contamination (American Petroleum Institute, 1972).

can be reduced, it has been shown by Chiou (1985) to have a significant effect on the adsorption of organic vapors. He states that the mineral fraction of a dry or slightly hydrated soil will be a powerful adsorbent for organic vapors at lower vapor pressures and that this may become the most important process in the uptake of organic compounds by mineral rich unsaturated soils. Figure 2.7 shows the impact of relative humidity on the adsorption of benzene and indicates a large increased adsorption as the relative humidity drops below 90 percent.

This relative humidity-adsorption phenomena may cause significant reductions in the amount of organic vapor measured at or near the soil surface. Thus, deeper soil gas probes would be advised for precautionary means (precluding the use of surface gas measuring devices). Probes located beneath a depth of 12 inches in almost all situations would encounter a saturated aqueous vapor, thus avoiding the increased adsorption phenomena shown in Figure 2.7.

(6) Shape and size of pores: Knowledge of the shape and size of pores or pore size distribution in soil is important in any understanding of the tortuous path vapors must traverse in reaching the soil surface. Figure 2.8 is a drawing of the possible variation in pore size an organic vapor might encounter. Note that some pores are totally blocked by interstitial water, and the rate of diffusion is thereby reduced by orders of magnitude. It is also worth noting here that the total porosity does not provide any indication of the pore size distribution. Nielson and Rogers (1982) using a mathematical model to estimate radon diffusion in earthen materials calculated the diffusion coefficient for radon by using nine pore size distributions. Figure 2.9 shows the impact various median pore sizes and water contents can have on the diffusion coefficient. In the drier range, a difference of an order of magnitude is observed in the diffusion coefficient, and Nielson and Rogers attributed this to the differences in the median pore size. Clayey soils tend to have a more uniform pore size distribution than do coarser soils (Hillel, 1971) whereas the coarse soils tend to have larger mean pore sizes which will transfer fluids faster under saturated conditions and vapors faster under unsaturated conditions. The diffusion

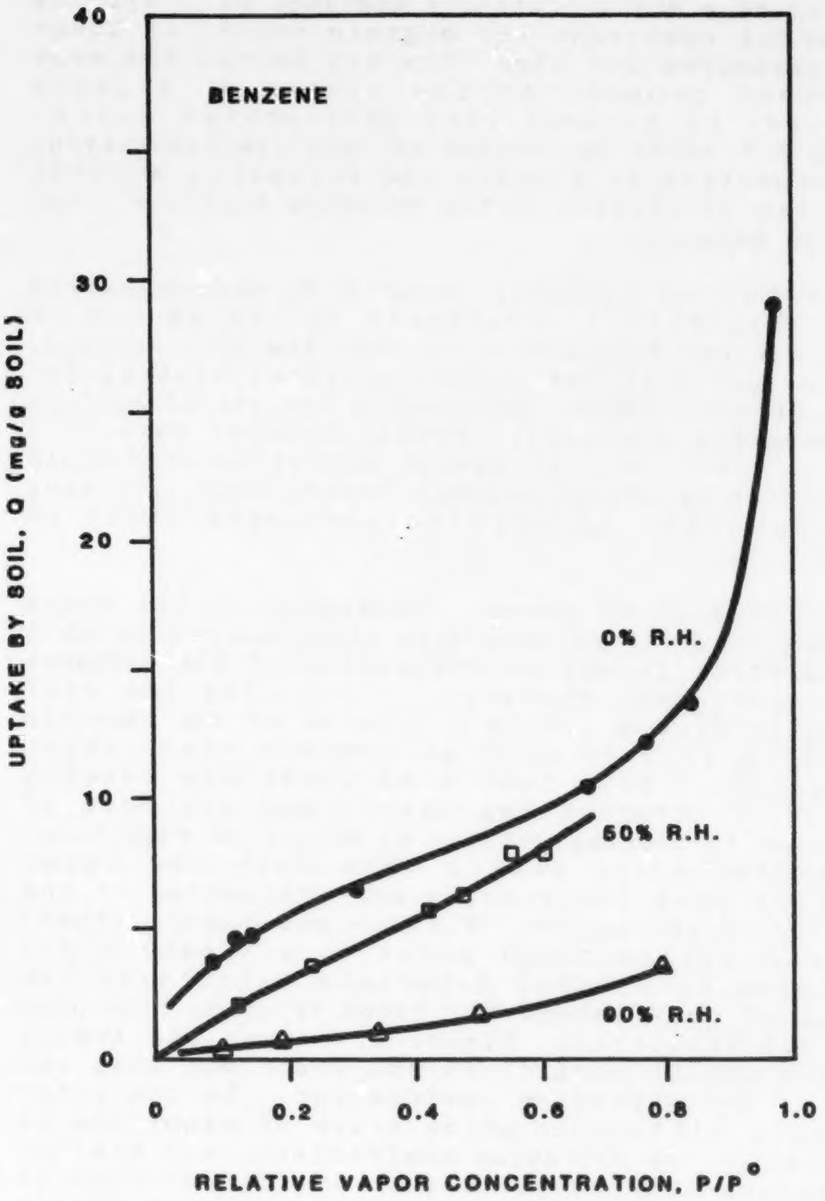


Figure 2.7. Benzene uptake by soil as a function of the relative vapor concentration, where P is the equilibrium partial pressure and P^0 is the saturation vapor pressure of the compound at the system temperature (Chiou, 1985).

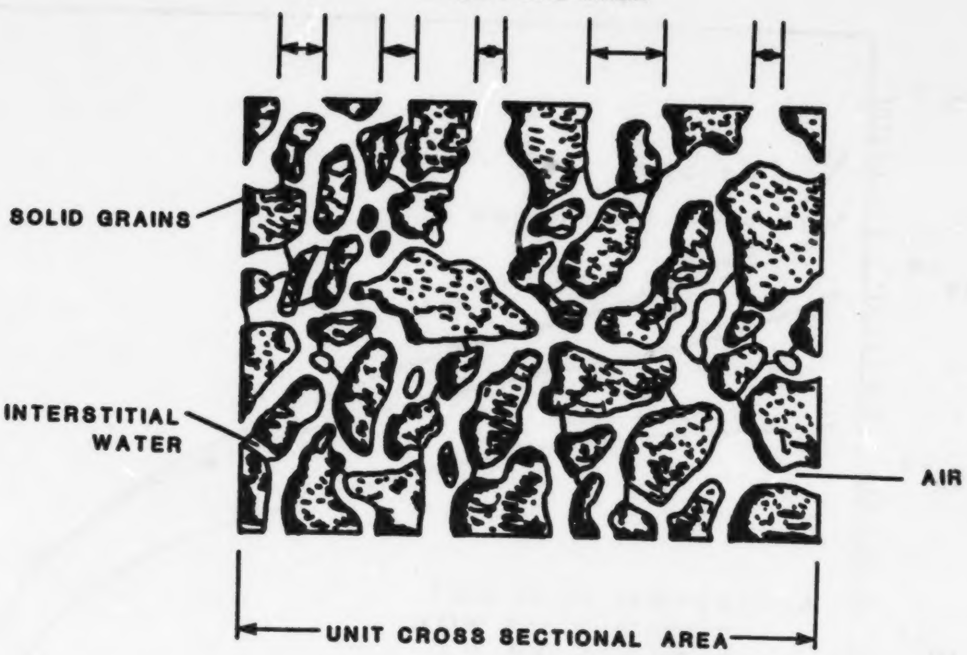

OPEN PORE AREA
SOLID GRAINS
INTERSTITIAL WATER
AIR
UNIT CROSS SECTIONAL AREA

Figure 2.8. Cross-sectional view of soil pore area (Nielson and Rogers, 1982).

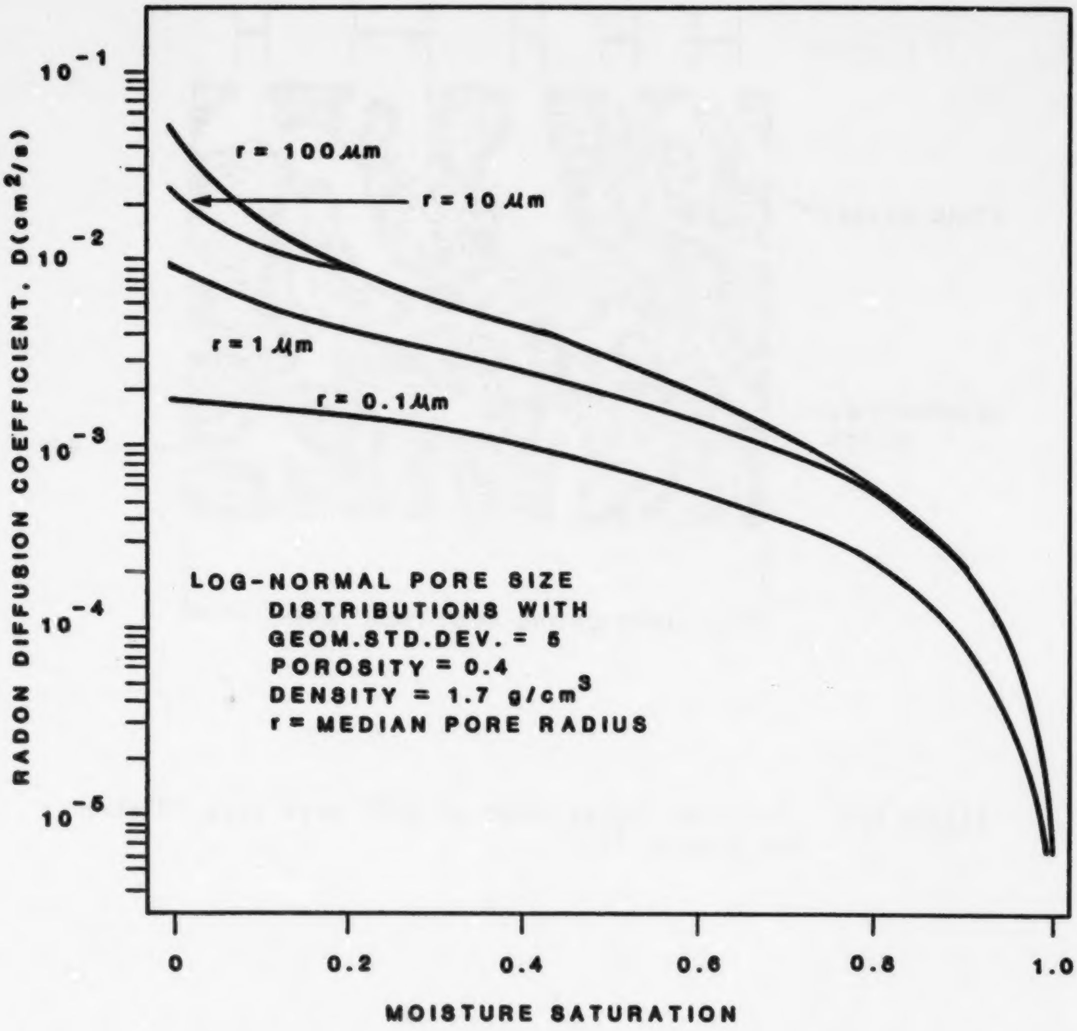


Figure 2.9. Comparison of diffusion coefficient moisture curves for various median pore sizes (Nielson and Rogers, 1982).

coefficient must ,therefore, compensate for this tortuous path for vapor flow; this is accomplished by replacing the diffusion coefficient with the effective diffusion coefficient (see chapter 3).

(7) Depth of unsaturated zone: Depth of the unsaturated zone or depth to the water table is a very important site parameter in soil organic vapor monitoring. Spreading of organic contaminants is enhanced by a shallow unsaturated zone as the opportunity time and volume for adsorption and retention is decreased. The shorter the vertical travel time is in the unsaturated zone, the greater is the opportunity for miscible organics to be dispersed into the ground water. [As the unsaturated zone increases in size (vertically and laterally), the possibility of textural changes and distinct horizontal layers forming is also increased.] [Deeper sampling might be recommended to avoid these discontinuities, which would alter the vertical vapor gradient.] Deeper sampling correlates to increased cost and to decreased convenience. In terms of vapor monitoring, a deeper unsaturated zone means a greater distance over which a vertical vapor gradient must be established. Thus, by the time vapors arrive at or near the soil surface from deep water tables, the concentration may be below detection levels and thus provide little information on the spatial extent of the plume. Successful vapor correlations under such conditions would require the concentration of the organic in the ground water to be exceedingly high and that the unsaturated zone be comprised primarily of coarse gravelly material.

(8) Retention: Depending on the solubility of the organic compound, the texture of the soil, and the pore size distribution, a certain percentage of the liquid contaminant will be retained in the soil pores. Column studies by McKee (1972) showed the specific retention of water to range from 10.37 to 17.67 percent in the soils he investigated whereas the specific retention of gasoline measured was only 6.10 percent. Other studies that he conducted showed that even after 844 pore volumes of water had passed through a column contaminated with gasoline, the effluent still had a gasoline taste. In another column McKee passed 3750 pore volumes of air and still could not completely vaporize the gasoline. The explanation for this comes directly from Figure 2.10, where Williams and Wilder (1971)

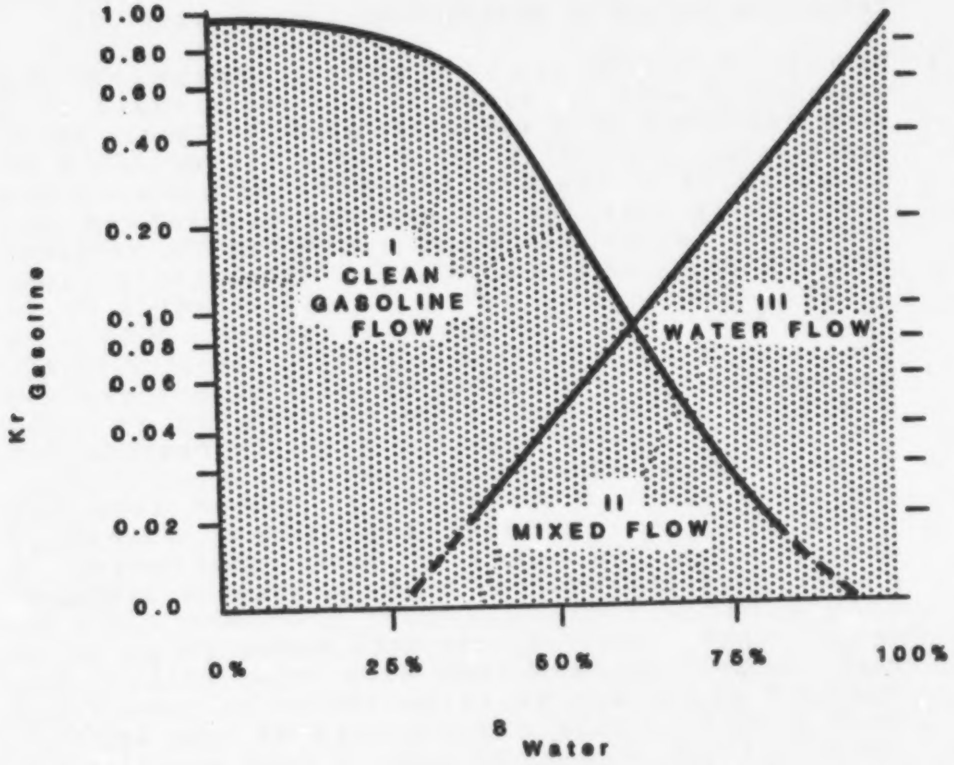


Figure 2.10. Relative permeability graph where S_{water} is the percent saturation of water and kr is the permeability ratio (ratio of observed permeability at a given saturation relative to the permiability at 100 percent saturation) (Williams and Wilder, 1971).

state that in region III little flow of gasoline will take place. This, they state, is because:

> "The smaller capillaries are filled with gasoline only when the pressure drop overcomes capillary forces. Thus until the pressure drop $P_{gas} - P_{water}$ is greater than $P_{capillary}$, it is impossible to move the snapped off gasoline bubbles through the throats (of the pore). As a result, the gasoline does not fill the neck or pore throat and thus becomes extremely difficult to move. The water which is used to flush the sand will therefore tend to flow through unblocked and continuous water filled channels rather than through the gasoline-blocked channels."

A continuous release of contaminant over long periods of time, because of this retention solubility factor, would make it increasingly difficult to describe the extent and the cause of the contamination as pulses might soon overlap.

(9) Temperature and temperature gradients: Soil temperature and the gradient that is established within the unsaturated zone can have an impact on the status of organic compounds. If great temperature gradients exist (surface layers), thermal diffusion will readily take place. Hillel (1971) indicates that "the effect of warming the soil is to lower the suction and raise the vapor pressure of soil water. Hence the effect of a thermal gradient is to induce flow and distillation from warmer to cooler regions." Thus, organic vapors migrating from the ground water to the soil surface during summer months and during the daytime will typically have to move against a temperature gradient (i.e., movement by concentration gradient) when they enter the surface horizon. During winter months when the soil surface may actually freeze, vapors would possibly be unable to escape and would therefore concentrate or be driven to move laterally. Organic compounds that have boiling points lower than soil temperatures will of course be highly volatile, such as the gaseous alkanes propane and isobutane which boil at-42.1°C and -11.7°C (see tables by Mackay and Shiu).

Soil temperature can also have a large impact on microbial growth. Cullimore (1982) states that lower soil temperatures tend to increase bacterial migration down through the soil and that Pseudomonads will actively degrade substrates (substances upon which enzymes act) under aerobic conditions if the ground water temperature is above six to eight degrees centigrade.

(10) Microbial influence: If conditions are optimum (pH, temperature, aeration, nutrients, detention time), the presence of microbial populations in the subsurface can lead to a significant biodegradation of organic compounds. The extent of biodegradation would be dependent on the number and species of micro-organisms reaching a critical level in relationship to the degree of difficulty in breaking down the compound in question. Table 2.7 gives a summary of the growth data for various micro-organisms on varying substrates in a study by Jamison et al. (1975). Note that no one organism thrived on all seven substrates and that no one substrate supported growth for all six micro-organism classifications.

A significant lag period is often required for the active microbial population to reach the optimum density. Wilson (1981) showed in his studies that a three-week lag period was required for the microbial community to shift in favor of nitrobenzene degrading organisms. Table 2.8 shows the fate of organic compounds applied to a sandy soil in the experiment by Wilson (1981). The results show that the substituted benzenes degraded to a much larger extent than the halogenated hydrocarbons.

The rate and extent of degradation is often controlled by oxygen (limiting factor) as the decomposition is primarily an oxidative process. Figure 2.11 by Baehr and Corapcioglu (1984) shows the influence of different levels of oxygen recharge on biodegradation rates. Raymond (1983) estimated that 3.5 pounds of oxygen were required to degrade 1.0 pound of gasoline hydrocarbons. Thus, the rate at which oxygen will diffuse through a subsurface horizon will control the rate of replenishment and thus the rate of decomposition.

If the concentration of the contaminant is too low, it may be below the minimum level required for maintenance of the micro-organism. However, Bouwer (1984) points out that the simultaneous utilization

TABLE 2.7. SUMMARY OF ORGANISM GROWTH IN VARIOUS SUBSTRATES

	Nocardia	Pseudo-monas	Acineto-bacter	Micro-coccus	Flavo-bacterium	Unclassified
n-Alkanes	+	-	-	+	-	-
Cyclic alkanes	-	-	-	-	-	-
Alkyl-substituted cyclicalkane	-	-	-	-	-	-
Monomethylakanes	+	-	-	+	+	-
Dimethylalkanes	-	-	-	-	+	-
Trimethylalkanes	+	+	+	-	-	+
Aromatics	-	+	+	+	-	+

+ Hydrocarbons utilized by micro-organism.

- Hydrocarbons not utilized by micro-organism.

(Jamison et al., 1965).

TABLE 2.8. FATE OF ORGANIC COMPOUNDS APPLIED TO A SANDY SOIL

Compound	Concentration applied	Volatilized	Column effluent	Degraded or not accounted for
	mg/liter	% of material applied		
Halogenated hydrocarbons:				
Chloroform	6.90	54± 9†	41± 4†	5±11†
	0.25	61±10	31± 9	8±14
Dichlorobromomethane	0.82	54±14	48± 4	- 2±17
	0.18	94±16	45±17	-39±18
1,2-Dichloroethane	0.81	49± 9	61± 9	-10±14
	0.25	50± 7	37± 5	+13±11
Tetrachloroethene	0.15	101±29	19±16	-20± 7
1,1,2-Trichloroethane	1.00	27±16	65±12	8±10
	0.16	47±13	61± 5	- 8± 7
Trichloroethene	0.90	58±14	28± 1	14±15
	0.18	88±18	21±13	- 9±11
Substituted benzenes:				
Chlorobenzene	1.04	27± 7	33± 9 (23± 4)‡	40± 7 (50±10)‡
	0.18	54±21	26±15 (34±24)	20±21 (12±13)
1,4-Dichlorobenzene	0.80	ND§	37± 4	63± 4
	0.13	ND	49±10	51±10
1,2,4-Trichlorobenzene	3.40	ND	46±11	54±32
	0.57	ND	39± 3	61±20
Toluene	0.90	38±11	2± 1.7	60± 8
	0.20	66±19	13± 6	21±15
Nitrobenzene	0.92	ND	80±29	20±25
	0.16	ND	60±20	40±31
Miscellaneous:				
Bis(2-chloroethyl)ether	0.86	ND	91±15	9±31
	0.16	ND	86± 1	14±20

†Means ±95% confidence intervals.
‡Material in effluent as determined by the purge and trap method.
§Not determined.
(Wilson, 1981)

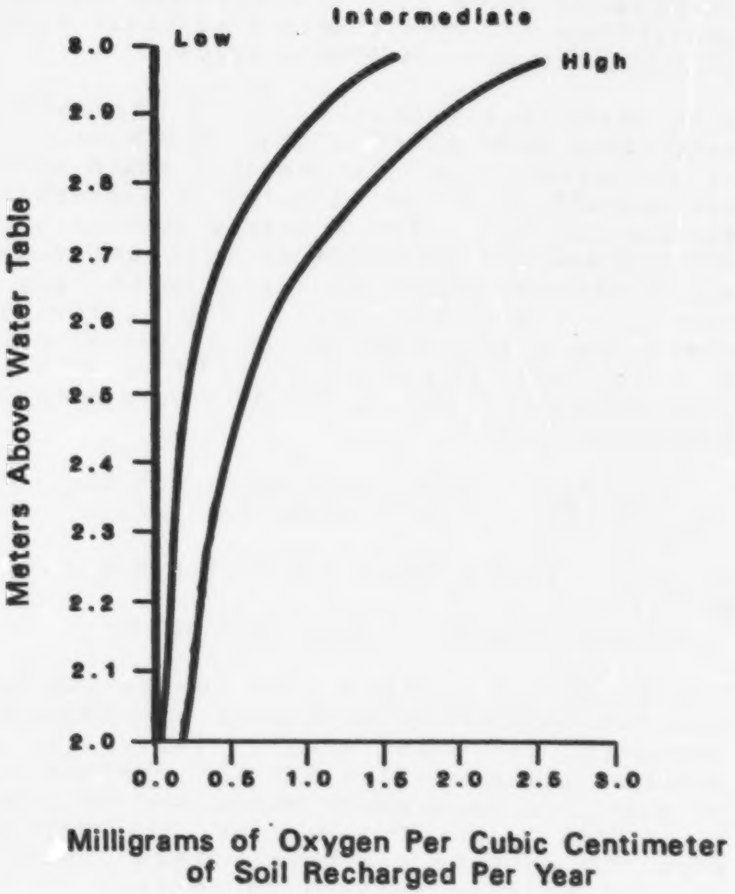
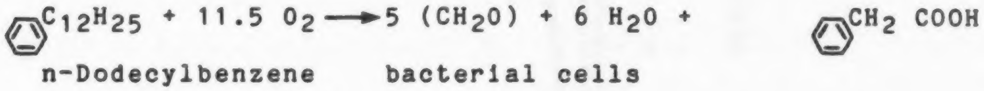


Figure 2.11. Biodegradation rate based on oxygen recharge (Baehr and Corapcioglu, 1984).

of several different substrates is possible (secondary utilization). Table 2.9 indicates that secondary utilization was possible for several non-chlorinated aromatic hydrocarbons and chlorinated benzenes in an aerobic biofilm. The halogenated aliphatics were not transformed under aerobic conditions but were nearly completely oxidized in a methanogenic biofilm (Table 2.10).

With petroleum products, it is the straight chain paraffinic hydrocarbons that are most susceptible to biodegradation; the branched chain paraffins and cycloparaffins follow in terms of susceptibility to biodegradation. The aromatic hydrocarbons and the non-hydrocarbon compounds of high molecular weight would be decomposed at the slowest rate (American Petroleum Institute, 1972). The following example shows the differences in the oxidative products for a straight chained paraffin hydrocarbon (hexadecane) and a cyclic hydrocarbon (n - Dodecylbenzene)

$$\underset{\text{hexadecane}}{C_{16}H_{34}} + 12.5O_2 \longrightarrow \underset{\text{bacterial cells}}{12(CH_2O)} + 4\ CO_2 + 5\ H_2O$$



The oxidative process with the cyclic hydrocarbon yielded oxidative products in addition to the bacterial cells and water. Table 2.11 gives the percent biodegradation for the various components of gasoline in a study conducted by Jamison, et. al. (1975). Note that benzene, toluene, and xylene were 100 percent degraded. Thus, these compounds may not be good tracers to monitor in the vapor phase under certain conditions.

In terms of organic vapor monitoring, the microbial influence may lead to situations where the contaminant is known to be in the ground water, but it is degraded in the aerobic unsaturated zone at a rate faster than it will diffuse to the surface. An additional problem may occur if ground water samples are taken directly from the aerobic zone that exists around wells; in such cases the microbial populations may be able to degrade the organic contaminant dissolved in the ground water (Cullimore, 1982) and thus give a false conclusion as to the extent of the plume. Finally, the

TABLE 2.9. AVERAGE UTILIZATION OF SUBSTRATES IN AEROBIC ACETATE-GROWN BIOFILM COLUMN AFTER ACCLIMATION

Substrate	Influent conc.* µg/L	Percent removal*
Primary		
acetate	1.0 mg/L	99.7±0.3
Secondary		
Chlorinated aromatics		
chlorobenzene	9.5±2.5	91±3
1,2-dichlorobenzene	9.6±2.4	97±1
1,3-dichlorobenzene	9.8±1.8	71±8
1,4-dichlorobenzene	10.8±1.8	99±1
1,2,4-trichlorobenzene	9.2±1.6	95±3
Nonchlorinated aromatics		
ethylbenzene	9.1±2	99±1
styrene	7.6±1.5	>99
naphthalene	13.8±3.5	99±1
Halogenated aliphatics		
chloroform	28.5±4.2	2±20
1,1,1-trichloroethane	15.9±3.3	5±27
tetrachloroethylene	9.8±3.7	2±40

*One standard deviation of the mean values is given (Bouwer, 1984).

TABLE 2.10. AVERAGE UTILIZATION OF SUBSTRATES IN METHANOGENIC ACETATE-GROWN BIOFILM COLUMN AFTER ACCLIMATION

Substrate	Influent conc.* µg/L	Percent removal*
Primary		
acetate	100. mg/L	93±2
Secondary		
Chlorinated aromatics		
chlorobenzene	22.±5	0±15
1,2-dichlorobenzene	15.±3	0±15
1,3-dichlorobenzene	10.±3	0±15
1,4-dichlorobenzene	10.±3	0±15
1,2,4-trichlorobenzene	11.±3	0±15
Nonchlorinated aromatics		
ethylbenzene	12.0±4	7±26
styrene	7.9±2	8±26
naphthalene	28.8±7	-2±29
Halogenated aliphatics		
chloroform	28.±7	99±1
carbon tetrachloride	17.±1	>99
1,2-dichloroethane	22.±3	-1±20
1,1,1-trichloroethane	18.±2	97±3
1,1,2,2-tetrachloroethane	27.±1	97±3
tetrachloroethylene	15.±4	76±10
bromodichloromethane	26.±3	>99
dibromochloromethane	25.±2	>99
bromoform	26.±2	>99
1,2-dibromoethane	27.±2	>99

*One standard deviation of the mean values is given (Bouwer, 1984).

TABLE 2.11. BIODEGRADATION OF THE COMPONENTS OF GASOLINE

Components of Sunoco 260	Initial concen-tration µlitre	Concentration at 192 hr. µlitre		Percent biodegraded over and above control
		Control	Sample	
n-Propane	Trace	Trace	Trace	0
n-Butane	0.63	0.37	0.37	0
n-Pentane	0.55	0.25	0.06	70
n-Hexane	1.36	0.78	0.15	46
n-Heptane	0.37	0.20	Trace	49
n-Octane	0.34	0.18	Trace	54
Olefins-C_4	0.11	0.18	0.12	0
Olefins-C_5	1.04	0.30	0.14	16
Olefins-C_6	0.51	0.16	0.07	18
Isobutane	0.11	0.13	0.12	0
Cyclopentane	0.17	0.05	0.04	0
Cyclohexane	0.12	0.06	Trace	45
Methylcyclopentane	0.41	0.18	0.14	10
Methylcyclohexane	0.05	0.04	Trace	75
2-Methylbutane	3.29	1.34	1.31	0
2-Methylpentane	1.72	0.83	0.73	6
3-Methylpentane	1.30	0.56	0.47	7
2-Methylhexane	0.74	0.53	0.36	23
3-Methylhexane	0.66	0.37	0.48	0
2-Methylheptane	0.35	0.15	Trace	38
3-Methylheptane	0.46	0.31	0.10	45
4-Methylheptane	0.15	0.08	Trace	48
2,2-Dimethylbutane	0.28	0.16	0.09	25
2,3-Dimethylbutane	0.86	0.37	0.36	0
2,2-Dimethylpentane	0.42	0.19	0.15	9
2,4-Dimethylpentane	0.53	0.31	0.25	11
3,3-Dimethylpentane	0.04	0.02	Trace	45
2,3-Dimethylpentane	0.48	0.24	0.21	0
2,5-Dimethylhexane	0.53	0.33	0.22	20
2,4-Dimethylhexane	0.46	0.22	0.20	0
2,3-Dimethylhexane	0.54	0.29	0.19	19
3,4-Dimethylhexane	0.09	0.08	Trace	84
2,2-Dimethylhexane	0.05	0.04	Trace	75
2,2-Dimethylheptane	0.09	0.06	Trace	62
1,1-Dimethylcyclopentane	0.12	0.04	Trace	25
1,2 and 1,3-Dimethylcyclopentane	0.12	0.10	Trace	78
1,3 and 1,4-Dimethylcyclohexane	0.02	Trace	Trace	0
1,2-Dimethylcyclohexane	0.16	0.05	Trace	26
2,2,3-Trimethylbutane	0.03	0.02	Trace	62
2,2,4-Trimethylpentane	3.47	2.40	1.95	13
2,2,3-Trimethylpentane	0.17	0.10	Trace	54
2,3,4-Trimethylpentane	1.89	1.22	0.97	13
2,3,3-Trimethylpentane	1.97	1.35	1.02	16
2,2,5-Trimethylpentane	0.51	0.35	1.02	23
1,2,4-Trimethylcyclopentane	0.03	Trace	Trace	0
Ethylpentane	0.08	0.05	0.04	0
Ethylcyclopentane	0.11	0.04	Trace	31
Ethylcyclohexane	0.06	0.06	Trace	95
Benzene	0.41	0.45	0	100
Ethylbenzene	1.36	1.61	0	100
Toluene	2.22	2.67	0	100
o-Xylene	1.62	2.18	0	100
m-Xylene	3.28	4.29	0	100
p-Xylene	1.03	1.31	0	100
Heavy ends	8.97	11.80	1.13	87

(Jamison, et al., 1975)

products that result from the oxidation process can sometimes be more soluble and toxic than the original compound.

HYDROGEOLOGIC PROPERTIES

(1) Ground-water flow (direction, velocity, gradient): Once a contaminant reaches the ground water, if it is soluble, its fate in terms of dispersal will then be controlled to a great extent by the direction and velocity of the ground-water flow. If the concentration of the contaminant is low and if the spill is small, the contaminant is quickly diluted by the process of mixing and diffusion so that a plume is difficult to delineate. However, "for most ground water flow regimes, mass transfer is predominantly diffusion controlled and therefore independent of flow rates. This is due to the generally low flow velocities in natural ground water flow fields" (Pfannkuch, 1984). Thus, knowledge of the direction of flow would most often be the deciding factor in the initial decision to locate gas probes and monitoring wells. Andres (1984) points out that well locations have sometimes been inaccurately located when the direction of ground water flow was predicted on the basis of the location of hydrologic boundaries and site topography.

For contaminants that reach the ground water but are immiscible in water (such as many petroleum products), the contaminant will follow the water table gradient. If a steep gradient exists, a greater interface will be developed, which will lead to a greater opportunity for the dispersal of slowly dissolving constituents into the ground water.

(2) Water Table Oscillations: Changes in the depth of the water table can have a large impact on vertical transport of contaminants. McKee (1972) observed a considerable rise in gasoline that had filtered down to the water table as the water table rose over a three year period. Oscillations in the water table could allow hydrocarbons that float to move over or under subsurface obstructions that might otherwise prevent their further migration. In an underground gasoline tank leak study in Montana, Reichmuth (1984) noted that when the water table was lower during the winter, a gravel layer

was exposed that possessed considerable void space. During the time of gravel exposure, Reichmuth suggested that gasoline vapors were transported by horizontal flow. That correlations of soil organic vapors with ground-water concentrations could be impaired by an oscillating water table is a possibility that grows out of Marin and Thompson's (1984) statement that changes in the water table level contribute to a vertical gradient that is not indicative of steady state.

(3) Lithology of the aquifer: Once a contaminant enters the confines of an aquifer, its further migration will be dictated to a great extent by the physical properties of the sediments that make up the aquifer (Figure 2.12) (American Petroleum Institute, 1972). Barriers to flow (retardation of flow) can occur if lateral changes take place in either texture (unconsolidated sediments) or rock formations (consolidated sediments). In sedimentary rocks, Osgood (1974) states that the orientation of the rock and the primary depositional characteristics of the unit are as important as permeability and porosity in dictating flow. The depositional characteristics would include such features as cementation and packing. In more steeply dipping rock units, Osgood (1974) suggests that the dominant flow direction of the hydrocarbons would be parallel to the strike, downslope, and that deviations from the strike direction would be controlled by jointing and fracturing. Non-uniform characteristics of the aquifer sediments would, of course, cause non-uniform advancement of the contaminant plume relative to the ground surface as water flow would be channeled through zones of lower resistance. If these sediments also comprised a large portion of the vadose zone, then organic vapors would also follow the path of least resistance and would move through the fissured and fractured rock according to the paths that were dictated. Lateral flow of vapors could be tremendous under such conditions and could thus negate any hopes for correlating the vapor concentrations with the ground-water concentrations. Schwille (1984) indicates that with fissured rocks, the gas tracer method would only be useful if the fissured rock were covered by a layer of porous loose rock.

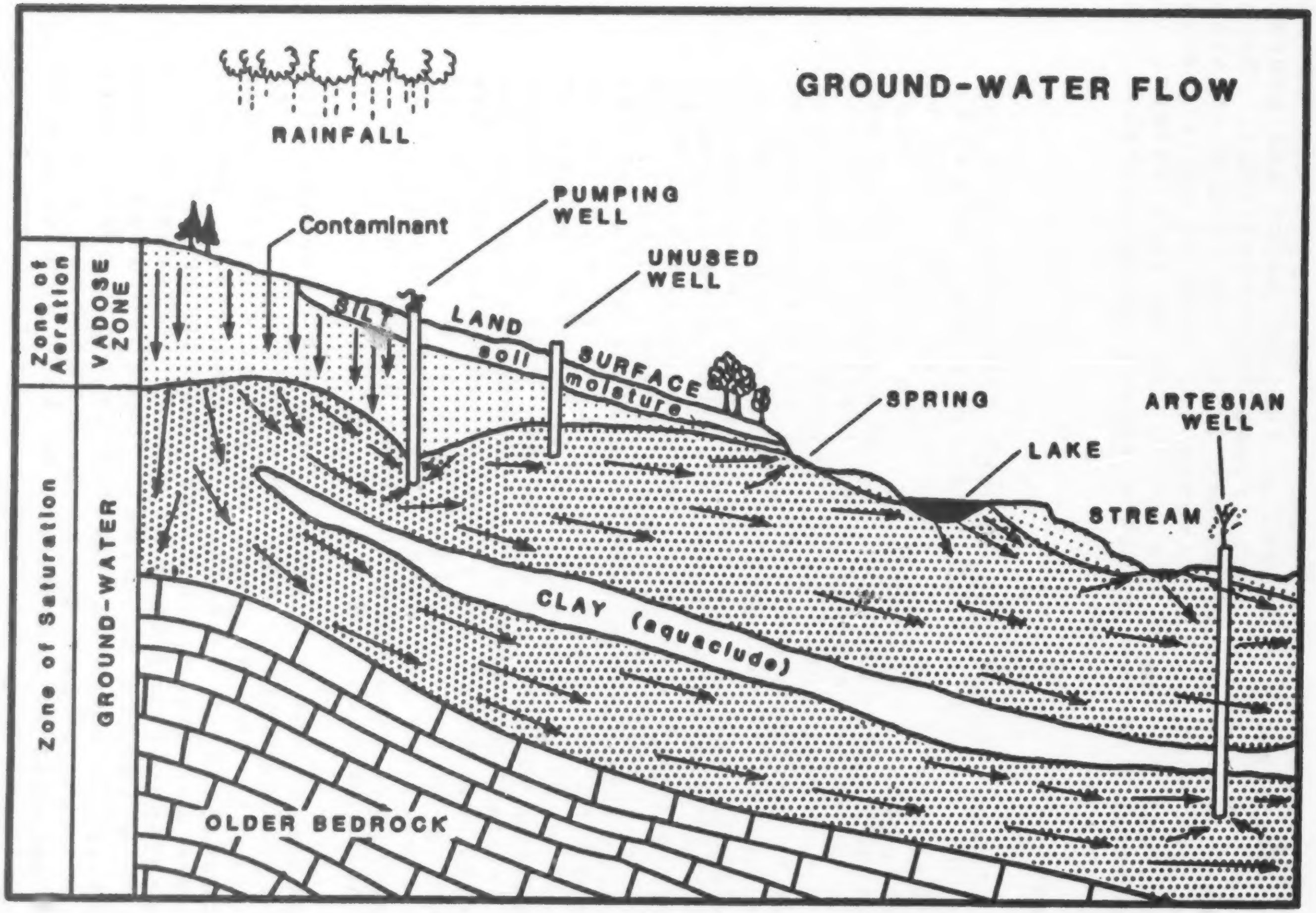

GROUND-WATER FLOW
RAINFALL
Contaminant
PUMPING WELL
UNUSED WELL
SILT
LAND SURFACE
soil moisture
SPRING
LAKE
STREAM
ARTESIAN WELL
CLAY (aquaclude)
OLDER BEDROCK
Zone of Aeration
VADOSE ZONE
Zone of Saturation
GROUND-WATER

Figure 2.12. Hypothetical ground-water system (American Petroleum Institute, 1972).

CHARACTERISTICS OF THE SPILL

Greater knowledge of the history of the spill can often provide the investigator with greater insight as to the proper location for soil gas probes (first approximation). Such characteristics as the total volume lost, the length of time the product was spilled (continuous vs. one-time spill), area of the spill, and the age of the spill, can be very helpful in better understanding the possible extent of unsaturated and saturated zone contamination.

MISCELLANEOUS

(1) Rainfall: Depending on the frequency and the amount of rainfall that occurs, organic contaminants in the unsaturated zone will be susceptible to leaching. In areas of high rainfall, oscillations in the ground water may occur which would bring contaminants closer to the soil surface. Obviously, any input of water will lead to decreased air-filled porosities and to reduced vapor movement. Vertical concentration gradients will be altered as vapors reaching the rainfall saturated zone will either concentrate, move laterally, or will be resolubilized to some extent. Vapor migration (upward, lateral) and resolubilization can lead to a wider spread of the contamination area. If the area in question is covered with vegetation, then the amount of leaching will be dependent not only on the amount of rainfall but also on the evapotranspiration, the amount of water in storage, and the effective rooting depth. Rainfall will also delay field measurements and make it extremely difficult to compare soil-gas concentrating before and after a rainfall event.

(2) Background water quality: The more contaminated the ground water, the more difficult it is to delineate the spatial extent of the particular contaminant in question. In some cases, several plumes may exist, that are partially or completely over-lapping and that represent different spills over a period of time. Greater instrument sensitivity would be required in those cases where the background contained numerous organic contaminants at concentrations that were orders of magnitude higher than the contaminant being monitored (see section on analytical methodologies).

(3) Barometric pressure and wind: Early work by Buckingham (1904) showed that changes in barometric pressure had little influence on soil gas transport in most cases, with its greatest influence on the gases in the soil pores at or near the soil surface. In a study conducted by Reichmuth (1984), gasoline vapors detected in a basement down gradient from an underground storage tank leak, worsened during periods of high wind and low barometric pressure. He concluded that such conditions were optimal for maximum earth out gassing . Other factors that would maximize this gas exchange would be the absence of vegetation (resistance to wind flow) and the presence of coarse permeable soil. However, one would have to conclude that in almost all cases, if soil gas probes were located several feet below the soil surface, the vertical vapor concentrations measured would not be influenced to any extent by this surface phenomena.

(4) Proximity to rivers, lakes, and pumping wells: The presence of rivers and lakes would mean that contaminants reaching the aquifer would be intercepted and dispersed even further (see Figure 2.13). Such interception of contaminant flow would mean an alteration in the subsurface boundaries of the contaminant plume. Another consideration is the proximity of soil-gas probes and monitoring wells to pumping wells as shown in Figure 2.13 (American Petroleum Institute, 1972). Altering the ground-water table by creating a cone of depression would cause immiscible organic compounds (floaters) to move laterally and deeper relative to the soil surface. This condition would not only alter the movement of a plume but also the distance over which a vertical soil gas gradient would have to be established.

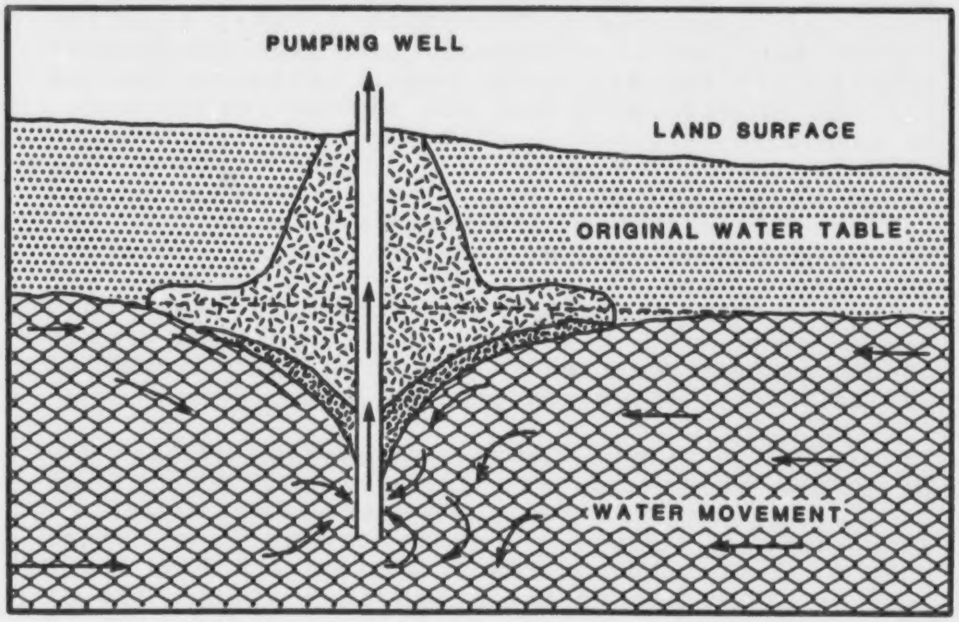

PUMPING WELL
LAND SURFACE
ORIGINAL WATER TABLE
WATER MOVEMENT

Figure 2.13. Diagram showing how oil on a water table can be trapped in a cone of depression created by draw-down of a pumping well (American Petroleum Institute, 1972).

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CHAPTER 3

TRANSPORT AND RETENTION OF DISSOLVED AND IMMISCIBLE ORGANIC CHEMICALS IN SOIL AND GROUND-WATER

INTRODUCTION

A large variety and quantity of different organic chemicals, some of which pose a health hazard, are accidentally or deliberately applied to soil where they may migrate to ground-water. For example, many different pesticides, mostly applied during agricultural operations, have appeared in the ground-waters in a number of different states (Pratt, et al., 1985). In addition, large numbers of dissolved organic compounds are accidentally released into soil from leaking waste disposal sites or storage tanks. These compounds migrate downward with flowing water and can enter and contaminate underground water supplies. A second large class of organic liquids found in soil are petroleum products which are released to soil by accidental leaks or large spills and which may be largely immiscible in water. These spills may occur from underground storage tanks which have either corroded, ruptured, or have faulty connections. Similarly, petroleum products might enter the soil when a tanker truck releases its contents in a highway accident.

In a complex soil, air, water and hydrocarbon system, an organic chemical compound, depending on its properties and on the soil conditions, may be found in a number of different phases: as an immiscible liquid, as a dissolved component of the soil-water solution, or as a gas. In addition, the immiscible liquid may be flowing or immobilized, and the dissolved components may be moving freely within soil solution or may be absorbed to soil mineral surfaces or to stationary organic matter in the soil. This chapter will provide an overview of the processes important in the transport and fate of organic contaminants in soil, focusing separately on (1) petroleum mixtures which are transported or retained in the soil as a fluid largely immiscible in water and on (2) soluble organic contaminants which dissolve readily in water and predominantly move by convection within flowing solution.

Movement of Liquid Oil Through Soil

When a large quantity of spilled oil is introduced at the soil surface, it will infiltrate under the influence of gravity principally as an immiscible fluid separate from water. The exact path and rate of the infiltration as well as the extent of lateral movement will depend in a complex manner on the permeability of the soil to water and oil, on the water and oil content, and on the presence of structural voids which contribute substantially to spreading of the spill. Although attempts are being made to formulate the oil and water transport problem mathematically (Baehr and Corapcioglu, 1984), quantitative values for the exact water and oil flow paths and flow rates in natural soils are for practical purposes unpredictable. Nonetheless, experimental observations, small column experiments, and model calculations which use simplifying assumptions have produced a general picture of the oil entry and transport process which describes the main features of a spill event.

Qualitatively, as oil enters the vadose zone it displaces air but not water from the pore spaces, and infiltrates vertically under the influence of gravity at a rate limited by the permeability of the oil-filled pore space. As the oil passes through a given region of the porous medium, it leaves behind a residual and largely immobilized concentration of insoluble oil which varies between approximately 5 and 20 percent of the void space depending on the type of oil and the characteristics of the soil (Dietz, 1970). Thus, if the total quantity of oil spilled into the soil is less than the amount required to fill the residual pore space in the vadose zone, then the body of the spill will not reach the ground-water and will remain in a pendular volume poised above the water table (see Figure 3.1A). If, however, there is an excess of insoluble oil, then part of the flowing oil will reach the ground-water where most of the remaining oil will spread into a thin film occupying the volume just over the saturated-unsaturated zone interface (see Figure 3.1B).

Stabilized Oil Spill Profile

After the transient infiltration phase has concluded, the insoluble oil body will be spread over a relatively fixed volume of soil which may or may not extend to ground-water. Those components of the oil body which are soluble will continually dissolve into the soil solution, and subsequently may migrate with flowing water. In addition, volatile components of the oil body exposed to soil air interfaces will evaporate into the soil air, and subsequently may migrate upward and laterally by vapor diffusion. The principles used

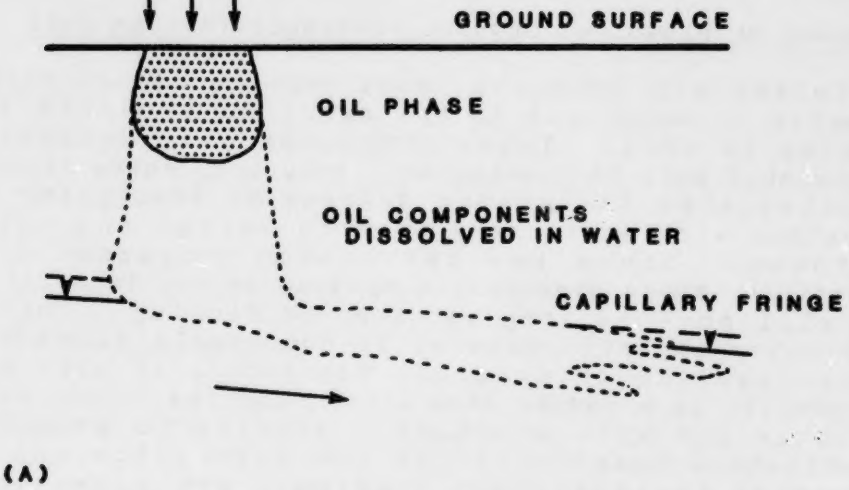

GROUND SURFACE
OIL PHASE
OIL COMPONENTS DISSOLVED IN WATER
CAPILLARY FRINGE
(A)

Figure 3.1. Oil migration pattern (Case No. 1) (Schwille, 1984).

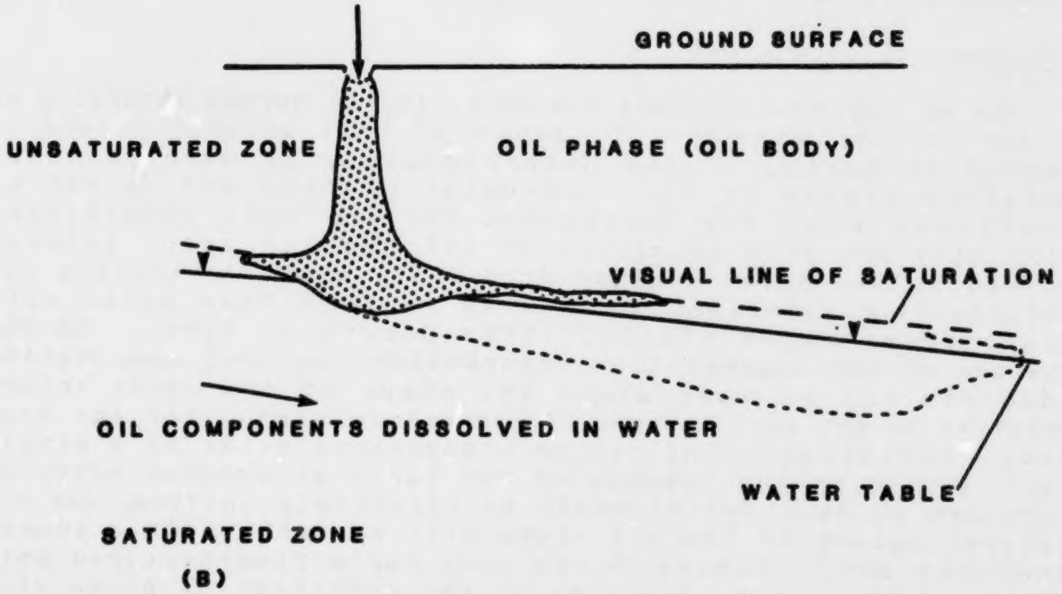

GROUND SURFACE
UNSATURATED ZONE
OIL PHASE (OIL BODY)
VISUAL LINE OF SATURATION
OIL COMPONENTS DISSOLVED IN WATER
WATER TABLE
SATURATED ZONE
(B)

Figure 3.1. Oil migration pattern (Case No. 2) (Schwille, 1984).

in quantifying these phenomena are discussed in the section describing transport processes.

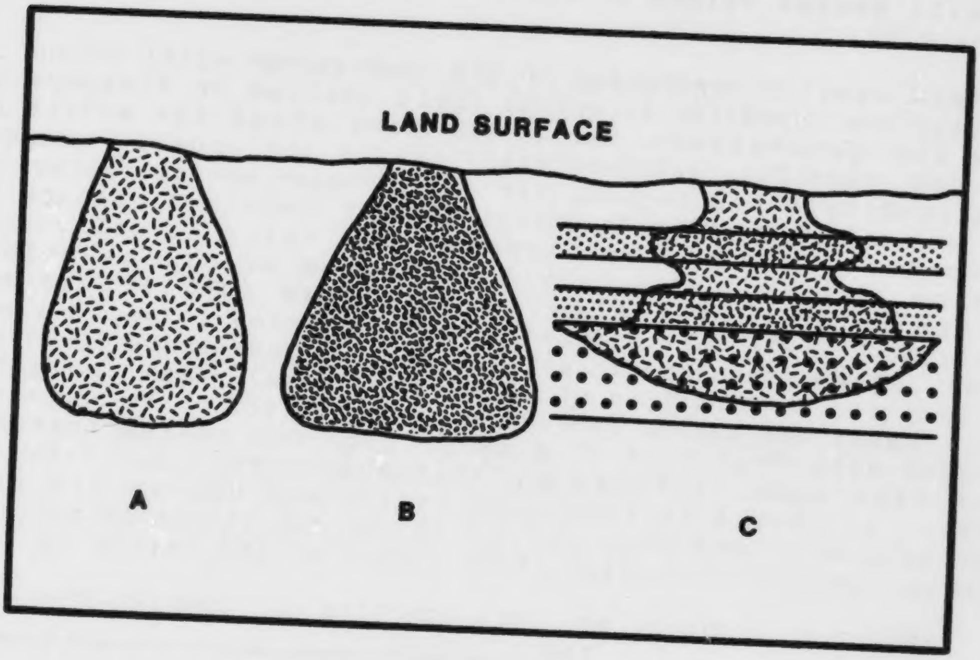
Movement of Dissolved Organic Chemicals Through Soil

Unlike oil products, many organic contaminants readily dissolve in water and do not exist as separate immiscible liquids in soil. These compounds move downward through unsaturated soil in flowing soil solution, where their movement is attenuated to varying degrees by adsorption-desorption reactions with stationary organic matter and soil mineral surfaces. Since the adsorption processes are largely reversible, these dissolved compounds do not immobilize in soil and will move as long as water is flowing. Thus, unless a particular organic compound is completely degraded by soil microorganisms or chemical reactions, it will only reside temporarily in a vadose zone which receives a net annual input of water and will eventually migrate to ground-water. A quantitative description of the adsorption and transport processes for dissolved chemicals are given in the next section.

PROCESSES GOVERNING TRANSPORT OF ORGANIC CHEMICALS THROUGH SOIL

Transport of Liquid Oil

As an oil spill enters the soil, it may spread laterally as it infiltrates downward. The extent of this lateral spread is highly dependent of the heterogeneity, permeability and moisture status of the soil-water profile and cannot be predicted with any confidence for any soil conditions. Virtually the only quantitative information about lateral spreading has been obtained from small scale laboratory oil infiltration experiments, usually in Hele-Shaw cells with transparent walls (Dietz, 1970; Schwille, 1984). In the absence of any quantitative information, several qualitative comments may be made about the shape of the spill volume relative to the soil texture of the vadose zone. For the most part, infiltration of oil in homogeneous soils of a single texture will in the absence of any large structural voids or barriers to vertical movement be relatively uniform, and the lateral extent of the oil plume will be smaller in a coarse textured soil (Figure 3.2A) than for a fine-textured soil (Figure 3.2B). The spreading of the infiltrating plume will continue with time and will produce a cone-shaped vadose zone profile until the plume reaches ground-water. If the soil is heterogeneous or layered, substantial lateral flow can occur at the boundary of a region of lower permeability where the oil will build up and flow laterally (Figure 3.2C). In addition, highly irregular plumes of oil may flow through fissures and cracks in bedrock or very impermeable soil and may produce a



A – HIGHLY PERMEABLE, HOMOGENOUS SOIL

B – LESS PERMEABLE, HOMOGENOUS SOIL

C – STRATIFIED SOIL WITH VARYING PERMEABILITY

Figure 3.2. Generalized shapes of spreading cones at immobile saturation (American Petroleum Institute, 1972).

complexly shaped volume of spilled material in the vadose zone (Figure 3.3).

Since spatial resolution of the hydrocarbon spill volume is generally too imprecise in actual field studies or cleanups to allow any generalizations to be made about the extent of spreading, specific idealized spill shapes are usually assumed in estimating the potential for ground-water contamination. A major assumption made in constructing this idealized picture is the concept that a fixed immobilized residual oil volume fraction, which depends only on the type of oil material, remains in the soil after a spill has infiltrated and stabilized. Table 3.1, adapted from information given in Dietz (1970), gives prototype values for the residual immobilized oil void fraction S_0 (fraction of total void space) remaining after an oil spill has passed through a volume of soil. In addition, residual void fractions of 0.05 or less for coarse textured soils have been reported by Pfannkuch (1983) and Schwille (1984). It should be cautioned that these values are only rough estimates and that actual values may differ in soils of different texture (Schwille, 1984). Part of the reason for the large variation in reported values for the residual oil void fraction is that the drainage of oil under gravity following wetting to a high degree of saturation is a dynamic process which is very rapid during the early stages and which undergoes a slow but continual decrease with time for many days after the initial rapid drainage (Figure 3.4). Thus, the residual oil content in soil after 5 days may be considerably higher than it is at 100 days. For this reason, the residual oil void fraction, S_0, should be regarded as an index similar to the water content "field capacity" which is very poorly defined in fine-textured soils (Hillel, 1971). Nevertheless, the residual oil content is a useful parameter for making rough calculations of the spatial volume occupied by a spill. For example, from an estimate of the residual void fraction percent, S_0, and the total porosity, ϕ, one calculates that a spill of volume, V_0, will eventually occupy a soil volume V_S where

TABLE 3.1. RESIDUAL OIL VOID FRACTION S_0 (ADAPTED FROM DIETZ, 1970)

Type of Oil	Residual Void Fraction
Light oil (gasoline)	0.10
Medium oil (diesel, light fuel)	0.15
Heavy oil (lube, heavy fuel)	0.20

$$V_S = V_0/\phi S_0 \qquad (1)$$

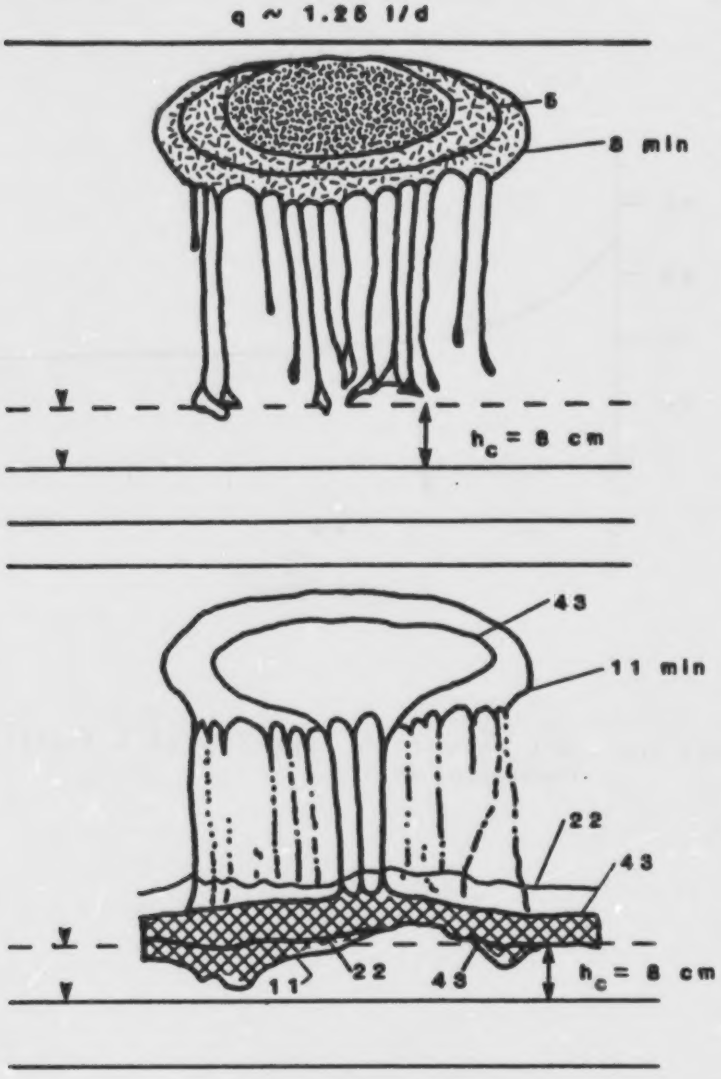

q ~ 1.25 l/d
5
8 min
h_c = 8 cm
43
11 min
22
43
22
11
43
h_c = 8 cm

Figure 3.3. Infiltration of kerosene into a porous medium through a narrow fissure at a rate 9=1.25 L/D. Capillary fringe height h_c is 8 cm.
Top: beginning stage
Below: after infiltration finished.
(Schwille, 1984)

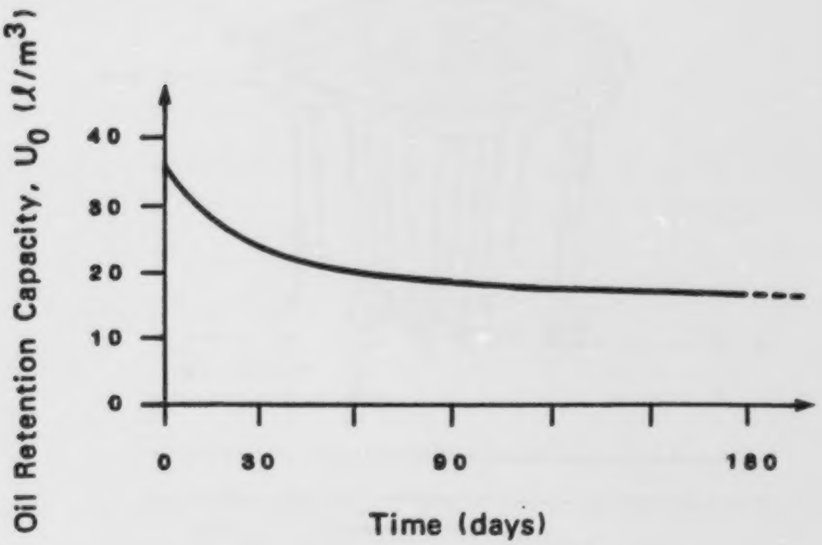


Figure 3.4. Oil retention capacity as a function of time (Schwille, 1975).

By making specific assumptions about the shape of the oil spill in the vadose zone, the amount of oil required to reach the ground-water may be calculated.

EXAMPLE

A gasoline truck spills 10,000 gallons (37.85 m^3) of gasoline ($S_0 = .10$) on the soil surface. The gasoline infiltrates over a surface area of 9 m^2. Calculate the volume of oil which will reach the ground-water table located at a depth of 30 meters assuming no lateral movement in the vadose zone. Assume that the soil porosity ϕ is 0.4.

Solution

The total volume of residual oil in the soil after stabilization may be calculated by using Eq. (1). Thus

$$V_S = (37.85\ m^3)/(0.4)(.10) = 946.25\ m^3$$

The total volume V_v occupied by the oil in the 30 m thick vadose zone, assuming no spreading (i.e., a cylindrical plume), is equal to

$$V_v = AL \qquad (2)$$

where A is the surface spill area (9 m^2) and L is the depth to ground-water (30 m). Thus, in this case $V_v = 270\ m^3$ and this volume is filled by a quantity $V_v \phi S_0 = 10.8\ m^3$ of oil, leaving 27.05 m^3 of oil to spread over the ground-water.

Accumulation Over Ground-Water

When the oil body reaches ground-water, the bulk of the material, which is less dense than water, will float on the surface of the ground-water interface and will spread out until the entire oil volume occupies a void volume fraction equal to S_0. The thickness, T, of the oil lens which has spread over the ground-water will depend on both the oil and soil properties but is generally roughly equated to the thickness of the water capillary zone (the zone above the water table where the water changes from saturation to field capacity) (Dietz, 1970). Table 3.2, taken from Dietz (1970), gives some rough estimates for the thickness of the oil film as a function of soil type. If the ground-water has no lateral velocity and the soil is homogeneous, the layer of oil should spread homogeneously over the ground-water and form a circular film. If the ground-water has a lateral velocity, the spill should be skewed in the direction of flow (Figure 3.5). The area, A_G, of the ground

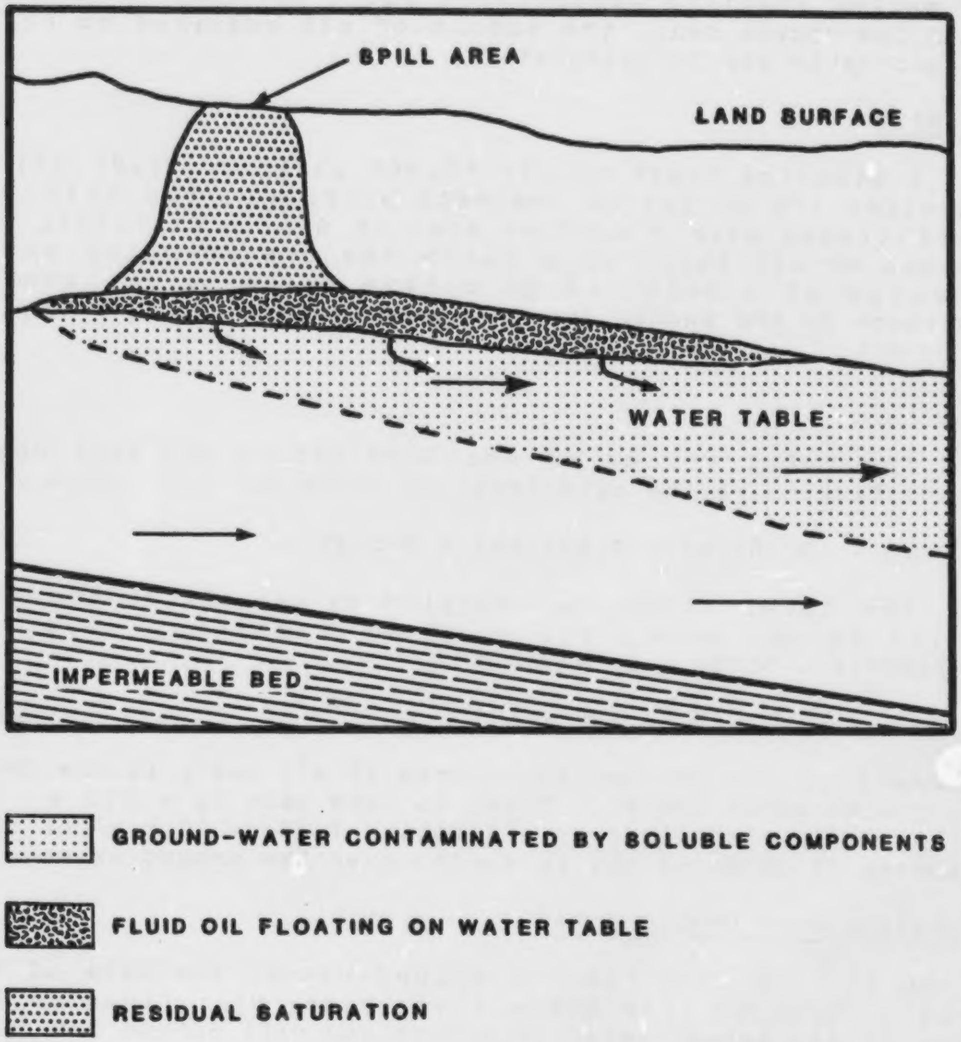

SPILL AREA
LAND SURFACE
WATER TABLE
IMPERMEABLE BED
GROUND-WATER CONTAMINATED BY SOLUBLE COMPONENTS
FLUID OIL FLOATING ON WATER TABLE
RESIDUAL SATURATION

Figure 3.5. Subsurface redistribution of a surface spill (American Petroleum Institute, 1972).

TABLE 3.2 OIL LENS THICKNESS ABOVE GROUND-WATER (AFTER DIETZ, 1970)

Type of Sand	Grain Diameter (mm)	Zone Thickness (cm)
Extremely coarse-very coarse	.5-2	2-9
Very coarse-moderately coarse	.2-.5	9-22
Moderately coarse-moderately fine	.05-.2	22-28
Moderately fine-very fine	.015-.05	28-45

water mound may be roughly calculated from the volume of oil, V_G, which reaches the ground-water using equation (3).

$$A_G = V_G/\phi T S_0 \qquad (3)$$

Estimates of the film thickness vary considerably among different researchers, in part because film thickness, like residual oil saturation, is a dynamic quantity which decreases slowly over time (Figure 3.6). Values given by Schwille (1967), largely obtained from model experiments, are generally of the order of 1 cm or less. Furthermore, the effective thickness of the oil lens may be altered by ground-water table fluctuations occurring during the time of lateral redistribution. This vertical motion can spread a layer of immobilized oil over a much greater vertical thickness than if the redistribution occurs over a motionless water table.

EXAMPLE (continued from above)

The 27.05 m^3 of oil which enters ground-water is assumed to form a symmetric circular film of thickness T = 0.01 m. Thus, using equation (3) the area of the film is $A_G = 67625\ m^2$. In this case, the film will form a circle of radius 147 m.

In practice, this estimate of lens thickness may be too small if ground-water level fluctuations are frequent in the area common to the spill boundary. For example, if the effective thickness of the film is increased to 0.1 meter, the A_G is reduced to 6763 m^2 and the radius of the spill over ground-water reduces to 46.5 m.

Transport of Dissolved Chemicals Through Soil

The most important processes governing transport of dissolved organic chemicals through soil are mass flow or convection of chemicals with flowing soil solution and hydrodynamic dispersion, the spreading of chemicals in soil by movement around solid obstacles. Many dissolved organic

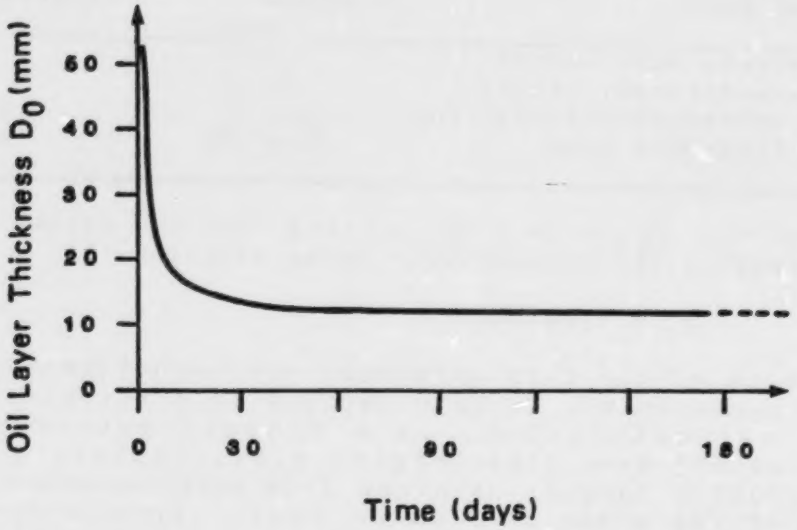


Figure 3.6. Relation between thickness of oil layer and spreading time (Schwille, 1975).

chemicals do not move freely in solution but are attenuated to varying degrees by reversible adsorption to stationary soil organic-matter and, to an extent, to clay mineral surfaces.

An important index for describing adsorption is the distribution coefficient K_d (cm^3g^{-1}) which is defined as the ratio of adsorbed concentration C_a ($\mu g\ g^{-1}$ soil) to dissolved concentration C_ℓ ($\mu g\ cm^{-3}$ solution) at equilibrium, or

$$C_a = K_d C_\ell \tag{4}$$

Another index which is defined as the distribution coefficient per unit soil organic carbon fraction f_{oc} (see Appendix) is called the organic carbon distribution coefficient, K_{oc} (cm^3g^{-1}), or

$$K_{oc} = K_d/f_{oc} \tag{5}$$

K_{oc} has been shown to vary less between soils than K_d for a given chemical (Hamaker and Thompson, 1972). Thus, it represents the adsorption potential of a given compound. Large compendia of K_{oc} values for pesticides and other organic chemicals are available in different references (Kenaga, 1980; Rao and Davidson, 1980; Jury, et al., 1984).

As a further attempt to standardize the adsorption potential of a given organic chemical, measurements have been made of the adsorption of compounds to octanol (Lambert, 1968). The octanol-water partition coefficient, K_{ow}, has been measured or calculated for a large number of organic chemicals (Rao and Davidson, 1980). Furthermore, various regression coefficients have been developed between K_{oc} and K_{ow}, including the relation

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18 \tag{6}$$

(used by Rao and Davidson, 1980) for 13 pesticides ($r^2 = 0.91$). Attempts have also been made to calculate K_{oc} or K_{ow} from more basic chemical properties or from chemical structure (Briggs, 1969). For example, Kenaga (1980) used the following regression with water solubility, C_ℓ ($\mu g\ cm^{-3}$),

$$\log K_{oc} = 3.64 - 0.55 \log C_\ell \tag{7}$$

to obtain K_{oc} values for a variety of organic compounds. He stated that the equation was accurate within 1.2 orders of magnitude.

In the Appendix it is shown that in a flowing solution, the average effective velocity, V_E, of a dissolved organic chemical which undergoes adsorption is:

$$V_E = J_w/(\rho_b K_d + \odot) = V_w/(\rho_b K_d/\odot + 1) \qquad (8)$$

Where J_w (cm D^{-1}) is water flux

ρ_b (g cm^{-3}) is soil bulk density

$\odot$ (cm^{-3}) is volumetric water content

and $V_w = J_w/\odot$ is pore water velocity

If a concentrated pulse or front of chemical is suddenly applied to the soil, not all of the molecules will move at the same velocity V_E because of dispersion. However, V_E will describe the average velocity of the pulse or equivalently, the velocity of the center of mass of the pulse.

EXAMPLE

Three compounds, chloride ($K_{oc} = 0$), benzene ($K_{oc} = 83$) and n-octane ($K_{oc} = 6800$) are introduced into an aquifer of porosity $\phi = 0.5$, water flux $J_w = 1$ m d^{-1}, bulk density $\rho_b = 1.5$ (g cm^{-3}), and organic carbon fraction $f_{oc} = .005$. Calculate the average travel time of these compounds to a well L = 1000 m downstream.

SOLUTION

When Eq. (5) is used, the K_d values of the three compounds (Chloride, benezene, n-octane) are ($K_d = f_{oc}K_{oc}$) 0, .415, 34 (cm^3 g^{-1}). From Eq. (8), this gives velocities V_E of 2.0, 0.89, 0.019 (m d^{-1}), respectively. The travel time, t, to move a distance, L, through the aquifer is simply $t = L/V_E$, or t = 500, 1124, and 5.26×10^4 days for chloride, benezene, and n-octane to reach the well.

The average travel times do not represent the earliest arrival times of the chemical pulse or front, which could be much shorter than the average time. Prediction of the earliest times requires a quantitative understanding of the soil geometry variations which is usually not possible to obtain in the field.

Also important in characterizing dissolved chemical transport is the degradation rate of the compound which in the absence of detailed information about specific reaction mechanisms is commonly represented by the half-life, $T\frac{1}{2}$ defined as the time at which the mass of the compound drops to 50 percent of its initial level while decreasing exponentially with time. For example, if a compound has a travel time to an observation well equal to twice its half-life, the mass at arrival should be degraded to ¼ of the initial mass at the time of injection. Table 3.3, adapted chiefly from Jury, et al. (1984), gives values of K_{oc} and $T_{1/2}$ for various organic chemicals together with a calculation of the travel time to reach 1000 m for the conditions given in the example above. In cases where the documented half-life is considerably smaller than the travel time, as for example with methyl parathion, it is unlikely that the compound will persist long enough to reach the well. However, it should be stressed that the ground-water conditions may differ considerably from the conditions under which the compound half-life was estimated.

The half-life and organic carbon partition coefficient represent so-called chemical benchmark properties for organic compounds. These single indices roughly describe the tendency to degrade and adsorb in soil systems. They mask much of the complexity of these processes and, for that reason, should be regarded as lumped parameters. Nevertheless, the values of these coefficients do provide valuable information about the possible behavior of the compound in the environment. For this reason, the benchmark properties are useful tools to use in screening large numbers of compounds and in placing them into smaller numbers of groups which behave similarly (Jury, et al., 1984). After such a screening process, experimental observations of specific chemical behavior may be used to make assessments of the expected behavior of other compounds in the same behavior group for which no direct experimental evidence is available.

Transient Movement of Dissolved Chemicals

From the above information, it is possible to make some general comments about a spill of chemical which is completely dissolved in water. The mass velocity of the chemical, retarded by adsorption compared to the velocity of the water, is roughly given by Eq. (8). The extent of lateral and vertical spread in the unsaturated zone, as in the case of an oil spill, is very dependent on specific soil conditions and cannot be predicted in detail with any certainty. General shapes such as those shown in Figures 3.1-2 for oil spills represent plausible profile shapes during vertical infiltration.

However, unlike the largely immiscible oil volume, the dissolved chemical mass does not immobilize in soil, and has no stabilized profile as long as water is flowing through the system. However, it may move very slowly downward because of

TABLE 3.3. K_{oc} AND $T_{1/2}$ VALUES FOR VARIOUS MISCIBLE ORGANIC CHEMICALS, ALONG WITH AN ESTIMATE OF THE TRAVEL TIME REQUIRED TO MIGRATE L = 1000 m THROUGH GROUND-WATER USING Eq. 8 WITH $J_w = 1 md^{-1}$, $\phi = 0.5$, $\rho_b = 1.5\ gcm^{-3}$, $f_{oc} = 0.005$

CHEMICAL	K_{oc} (cm^3g^{-1})	$T_{1/2}$ (d)	TRAVEL TIME (yr)	REFERENCE
ATRAZINE	160	71	4.6	A
BENZENE	83	*	3.1	A
BROMACIL	72	350	2.8	A
CARBON TETRACHLORIDE	110	*	3.6	A
CHLORIDE	0	∞	1.4	
DDT	2.4E5	3800	4900	A
DIELDRIN	12000	868	250	A
EPTC	280	30	7.1	A
EDB	44	*	2.3	A
LINDANE	1300	266	28	A
METHYL PARATHION	5100	15	106	A
MONURON	180	166	5.1	A
NAPROPAMIDE	300	70	7.5	A
NAPTHALENE	1300	*	28	A
NITROBENZENE	71	*	3.6	A
N-OCTANE	6800	*	141	A
PARATHION	11000	18	227	A
PHENANITRENE	23000	*	474	A
PHENOL	27	*	1.9	A
PHORATE	660	82	14.9	A
PROMETRYN	610	60	13.9	A
SIMAZINE	140	75	4.2	A
TCE	150	*	4.5	B
1,1,1-TRICHLOROETHANE	113	*	3.7	B
TRIALLATE	3600	100	75	A
TRIFLURATIN	7300	132	152	A
VINYL CHLORIDE	400	*	9.6	A

* no value available
A Jury, et al., 1984
B Josephson, 1983

adsorption reactions or may cease to move entirely if the water input to the soil is stopped for a prolonged period of time and the chemical is below the first few meters where it might migrate upward with water moving towards a dry soil surface.

Oil Migration After Stabilization

When the liquid oil phase is stabilized in the soil, the immiscible oil body shares a large interface with the surrounding liquid water. Thus, any water percolating through an oil spill either in the saturated or unsaturated soil-water zones will pick up dissolved components from the oil-water interface and will carry them downstream at the end of the spill. Fried, et al. (1979), analyzing experimental results and applying theoretical calculations, concluded that water percolating through a body of immobilized spilled oil will reach saturation levels with respect to the dissolved components after a short period of time or equivalently after a short travel distance, of the order of several tens of centimeters. Thus, in a region where water is flowing, the oil spill acts as a distributed source of dissolved organic chemicals as long as the immiscible material remains in place. Once present as a dissolved component of water, the organic compound is transported by convection and dispersion in the manner described in the previous section.

To obtain rough estimates of the release of chemical from the stabilized spill into ground-water, one may neglect hydrodynamic dispersion and write the mass flux, J_s, of dissolved chemical as the product of the water flux, J_w, and the saturated concentration of organic C_ℓ (g m^{-3})

$$J_s = J_w C_\ell \tag{9}$$

This equation together with knowledge of ground-water flow rates and oil component solubilities may be used to roughly estimate the flux of dissolved material from the residual spill into the ground-water.

EXAMPLE

For illustration, the previous example is used where a gasoline spill spread into a thin 1 cm thick film over the ground-water and covered a radius of 147 m. When Figure 3.7 adapted from Somers (1974) is used, the solubility of the gasoline mixture is roughly estimated as $C_s = 10$(mg ℓ^{-1}) = 10 (g m^{-3}). Assume that the aquifer has a ground-water velocity of $V = 2$ (m d^{-1}) and a water-filled porosity of $\phi = 0.4$. Thus, the ground-water flux is $J_w = \phi V = 1$ (m d^{-1}).

As the ground-water flows under the spill, it will pick up dissolved components until, at the downstream edge, a layer of flowing ground-water containing dissolved gasoline components is formed (see Figure 3.5). The width of this zone of chemical will depend on the extent of vertical migration by diffusion and dispersion of dissolved material below the spill into the ground-water, which may be roughly estimated from known information about transverse dispersion coefficients. Dissolved chemical in this zone perpendicular to the ground-water flow direction will decrease in concentration at greater ground-water depths

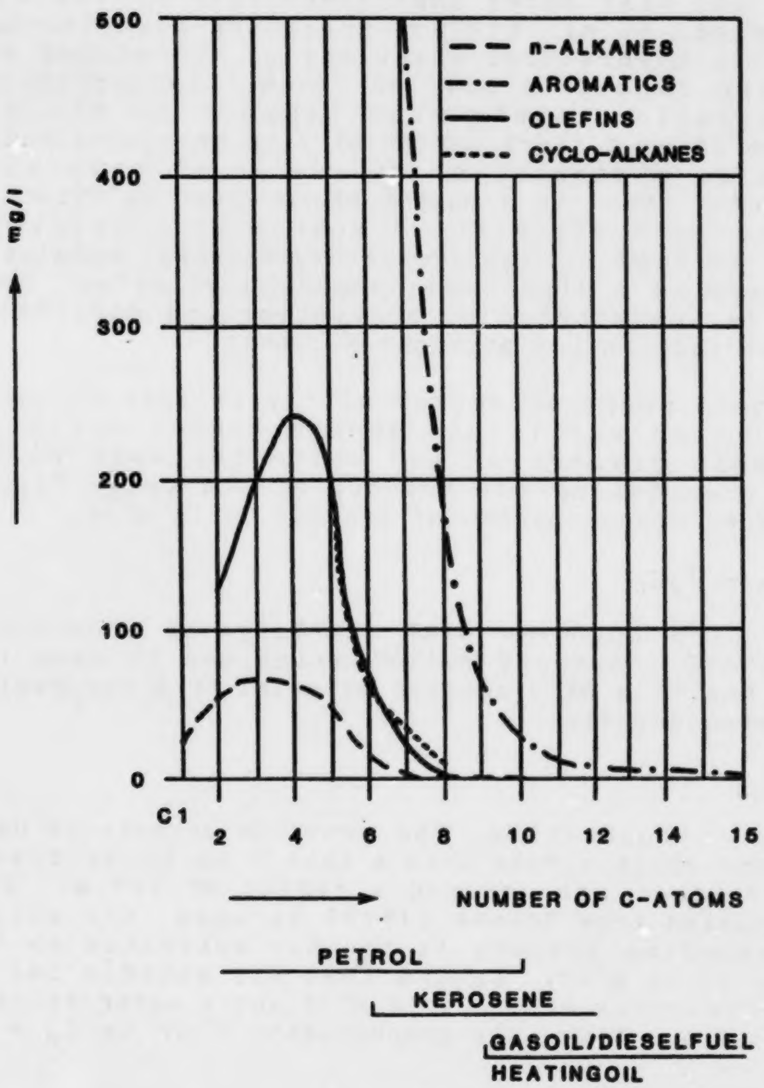


Figure 3.7. Solubility of hydrocarbons in water (Somers, 1974).

because of dispersion. Fried, et al. (1979), in order to produce a simple conceptual model of the release of chemical from the spill, defined an equivalent dissolved chemical layer thickness, D, which contained the same total mass of chemical as the actual profile but which had all of the chemical at the saturated solubility concentration (see Figure 3.8).

In analyzing this problem by using a two-dimensional form of the dissolved chemical transport equation (A.14 in the Appendix), Fried, et al. (1979), calculated that the equivalent thickness, D, in ground-water below the oil lens containing a saturated concentration of the dissolved chemical was on the order of 1 m for the spill geometry given in the previous example. In the example discussed above, the gasoline spill formed a circular pancake of radius R in contact with ground-water. Thus, by using the ideal model of Fried, et al. (1979), we calculate that the front of dissolved chemical flowing in the ground-water as it leaves the spill region will be approximately 1 m deep and 2 R wide (plus a small amount of additional lateral width from dispersion). By using Eq. (8), we can estimate the mass flux of dissolved chemical as $J_s = J_w C_e = 10$ (g $m^{-2}d^{-1}$). The cross-sectional area of flow is $A = 2RD = 294$ m^2 since R = 147 m. Thus, the spill discharges the dissolved chemical into the ground-water at a rate $Q = J_s A$ = 2940 (g d^{-1}) or Q = 1073 (kg yr^{-1}). Since the total mass of the spill in ground-water (assuming a density of 900 kg m^{-3}) was about 27.05 m^3 x 900 = 25000 kg, this discharge rate would trasnsfer about 1/23 of the spill to the ground-water in one year. This would dissolve the spill in about 23 years if the entire spill volume were equally soluble and if the lateral extent of the spill remained unchanged.

Obviously, the extent of dissolution into ground-water is much greater when the layer of oil at the ground-water interface is spread thinly over the surface than if the immobilized layer is thicker and has a smaller contact area with ground-water. In the second case from an earlier example, the spill thickness was increased to 10 cm which decreased the spill radius to 46.5 m. If all calculations above are repeated, the thickness, D, of the dissolved organic zone at the exit boundary calculated by the method of Fried, et al. (1979), drops to about 0.70 m, and the dissolved chemical mass flux decreases to 238 kg/yr. At this rate of dissolution, it would require over 100 years to remove the residual spill if the dissolution process and area extent remained constant during the lifetime of the oil event in the soil.

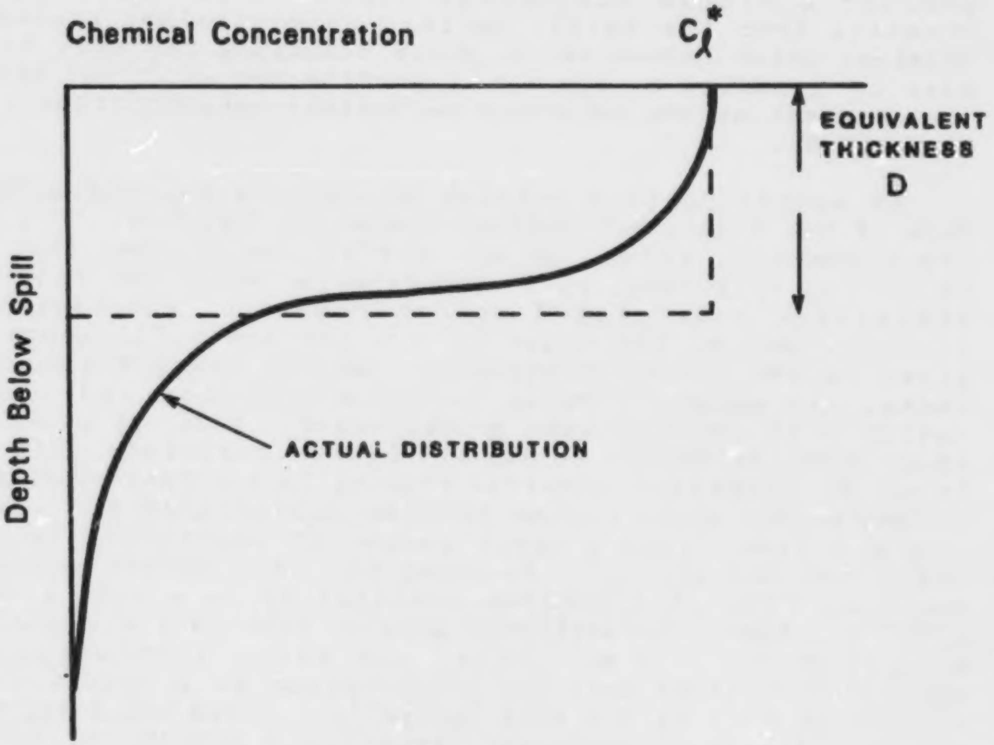

Chemical Concentration
C_ℓ^*
EQUIVALENT THICKNESS
D
Depth Below Spill
ACTUAL DISTRIBUTION

Figure 3.8. Comparison of actual and idealized concentration depth profiles below a waste spill in ground water. The equivalent thickness, D, is defined so that the rectangle has the same area between the axes as the curve. (i.e., the same mass of chemical). C_ℓ^* is the chemical solubility in water.

Oil Dissolution Within the Vadose Zone

Water percolating downward through the portion of the vadose zone volume contaminated by the residual portion of the oil spill will also dissolve into solution, creating a new source of dissolved oil material to contaminate ground-water. The extent of mass flow from this source will depend on the spill shape, the percolation rate, and the extent of lateral migration of the dissolved material. This mass flow rate is too uncertain to be estimated quantitatively unless the spill shape is known. As a rough estimate, the mass flux may be calculated as the product of water percolation rate, solubility, and the spill cross-sectional area normal to flow in the vadose zone. In the case of the previous example, assuming 1 ($m\ yr^{-1}$) vertical drainage through the spill and $A = 9\ m^2$ area, the calculated mass flux is $J_w C_s^* A = .09$ ($kg\ yr^{-1}$) which is very small compared to the release rate into the ground-water. This is because the interfacial area between undissolved oil and water is very much larger in the latter case and because the drainage flux is much smaller than the ground-water flux.

Sinking of Heavy Insoluble Components into Ground-Water

Organic liquids which are immiscible in water and denser than water could sink through the saturated ground-water zone if not bound in a residual state (Anderson and Jones, 1984; Mackay, et al., 1985). There has been some laboratory evidence of this phenomenon (Schwille, 1975), and it probably contributes to the vertical transport of material within the saturated zone. These "sinkers" as they are called could eventually reach the bottom of the aquifer if they are not immobilized en route (Mackay, et al., 1985).

MOVEMENT OF HYDROCARBON VAPOR THROUGH SOIL

The volatile components of the oil material will release chemical to the vapor phase which will in turn migrate toward the soil surface by diffusion (lateral and vertical) or will sink through the soil air if the partial pressure of the vapor is sufficiently high and if the vapor is denser than air. The rate of migration will be a function of the soil resistance to vapor flow, of the amount which is redissolved into the liquid phase, and of the amount which is adsorbed or degraded. The mathematical description of the transport process, described in detail in the Appendix, combines a mass balance (Eq. A.1) with the flux equation for vapor movement called Fick's Law (Eq. A.4).

Equation (A.4) describing vapor flux assumes that vapor is transported only by diffusion, and this is a reasonable approximation if the air phase is stagnant and if the chemical vapor is a dilute component of the soil atmosphere. However, some mass flow of vapor could occur, particularly if a large quantity of chemical vapor which is denser than air is evolving in the unsaturated zone. In this case, the overlying dense vapor could sink as well as diffuse through the air phase and would collect at the ground-water interface (Schwille, 1984).

Although chemical transport occurs in the vapor phase when mass flow of dissolved chemical compounds is negligible, chemical vapor molecules still interact with the liquid and adsorbed phases by redissolving when the molecules come into contact with water which is low in dissolved concentration. The relationship which describes the equilibrium partitioning between the vapor and liquid concentrations is called Henry's Law:

$$C_v = K_H C_\ell \qquad (10)$$

where K_H ($\mathrm{cm^3}$ solution/$\mathrm{cm^3}$ air) is the dimensionless form of Henry's constant (Jury, et al., 1983). Since Henry's Law has been shown to be valid all the way to saturation for a number of organic chemicals (Spencer and Cliath, 1970), it is commonly calculated as the ratio of saturated vapor density, C_v^*, to water solubility, C_ℓ^*. Values of C_c^*, C_ℓ^*, and K_H for a number of organic chemicals are given in Table 3.4.

The Henry's Law constant is also expressed occasionally as a ratio of vapor pressure to dissolved concentration, as, for example, in

$$P_v = k_H C_\ell \qquad (11)$$

where P_v (Pa or J $\mathrm{m^{-3}}$) is vapor pressure, and k_H has the units of ($\mathrm{Pa\text{-}m^3 g^{-1}}$). The conversion factor between k_H and K_H in Eq. (10), obtained by using the ideal gas law is:

$$k_H = K_H \frac{RT}{M} \qquad (12)$$

where $R = 8.3$ ($\mathrm{J\ mole^{-1} {}^\circ K^{-1}}$) is the universal gas constant, T is the absolute temperature, and M (g $\mathrm{mole^{-1}}$) is the molecular weight of the compound. An extensive compendium of values of k_H for a variety of organic chemicals are given in Mackay, et al. (1982).

As shown in the Appendix, the effective soil vapor diffusion coefficient for an organic chemical which is also present in the adsorbed and dissolved phases is reduced, often significantly, compared to the diffusion coefficient of a gas which is insoluble. Gas dissolution and subsequent adsorption has the effect of greatly slowing down the transport of the chemical in the vapor phase and also of exposing the gas molecules to degradation processes which may only be occurring in solution. However, the Henry's Law partition model Eq. (10) implies that the vapor concentration is proportional to the dissolved concentration (and, as shown in the Appendix, to the total concentration). Thus, to the extent that the equilibrium relations are valid in soil, the vapor phase concentration may be used to quantitatively monitor a volatile waste spill. Furthermore, even if the relationships are only approximately valid because of rate-limited nonequilibrium between phases, the vapor phase profile will still give qualitative information useful in detecting a spill and mapping its spatial extent.

Diffusion Travel Times

For any spill with volatile components, a vapor phase will evolve above the dissolved phase as it migrates through ground-water. The maximum vapor concentration will be given by Eq. (10) where C_ℓ is the concentration of dissolved organic material at the ground-water interface with the vadose zone. This vapor will move upward through the vadose zone by diffusion (reduced by dissolution and adsorption), by possible microbial degradation, and by chemical transformations.

A qualitative measure of diffusion for a given chemical, called the characteristic diffusion time, t_D, is the time required for an organic chemical with an effective diffusion coefficient, D_E, to diffuse through a distance L (Jury, et al.,1983):

$$t_D = L^2/D_E \tag{13}$$

where D_E is given by Eq. (A.17) of the Appendix. Table 3.5 summarizes values of t_D to diffuse L = 1m, calculated by using the procedures in the Appendix.

The values in Table 3.5 are qualitative but do allow compounds to be grouped into mobile and relatively immobile categories of vapor diffusion potential. Thus, for example, ethylene dichloride has a relatively high saturated vapor density (Table 3.4) but only a modest vapor mobility because so much of its total mass partitions into dissolved and adsorbed phases. Conversely, n-octane, with even lower vapor density,moves much faster because of its low solubility.

Steady-State Diffusion Profiles

For those compounds with reasonably short diffusion times, the vapor concentration profile with depth should reach a

TABLE 3.4. SATURATED VAPOR DENSITY, WATER SOLUBILITY AND HENRY'S CONSTANT K_H FOR VARIOUS VOLATILE AND SEMIVOLATILE ORGANIC CHEMICALS

Chemical	Saturated Vap. Density	Water Solubility	Henry's Constant	Reference*
	(gm^{-3})	(gm^{-3})	(K_H x10^4	
Benzene	400	1.8E3	2200	A
Biphenyl	0.49	7.5	600	A
Carbon Tetrachloride	750	8.0E2	9400	A
Chlorobenzene	71	4.7E2	1500	A
Chloroform	960	8.0E3	1200	A
Chloromethane	1.2E4	5.4E3	22000	B
DDT	6.0E-6	3.0E-3	20	A
Dieldrin	1.0E-4	1.5E-1	6.1	A
EPTC	0.22	3.7E2	5.9	A
EDB	120	3.4E3	350	A
Ethylene	4.7E4	1.3E2	3600000	C
Ethylene Dichloride	320	8.0E3	400	C
Lindane	1.0E-3	7.5E2	1.3	A
Methyl Bromide	2.0E4	1.3E4	15000	A
Napthalene	1.6	3.2E1	500	A
Nitrobenzene	1.8	1.8E3	1000	A
N-Octane	94	6.6E-1	1400000	A
Phenol	0.57	8.2E4	16	A
Trifluralin	2.0E-3	0.3	67	A
TCE	440	1.0E3	4400	C
Toluene	150	5.2E2	3000	B
1,1,1-Trichloroethane	1.4E3	9.5E2	15000	C
Vinyl Chloride	8.7E3	9.0E1	970000	A

*A = Jury, et al., (1984)
B = Mackay, et al., (1982)
C = Thomas (1982)

TABLE 3.5. TIME TO DIFFUSE L = 1 m THROUGH A SOIL
WITH Φ=0.5, a=0.3, D_V^{air}=4300 cm^2/d
f_{oc}= .005 USING eq 6 AND (A17)

	K_{OC} (mℓ/g)	K_H -	T_D (d)
Benzene	$8.3x10^1$	$2.2X10^{-1}$	129
Biphenyl	$1.4x10^3$	$6.6x10^{-2}$	5100
Carbon Tetrachloride	$1.1x10^2$	$9.4x10^{-1}$	45
Chlorobenzene	$1.5x10^2$	$1.5x10^{-1}$	292
Chloroform	$2.9x10^1$	$1.2x10^{-1}$	121
Chloromethane	$3.9x10^1$	2.2	16
DDT	$2.4x10^5$	$2x10^{-3}$	$2.9x10^7$
Dieldrin	$1.2x10^4$	$6.7x10^{-4}$	$4.2x10^6$
EPTC	$2.8x10^2$	$5.9x10^{-4}$	$1.1x10^5$
EDB	$4.4x10^1$	$3.5x10^{-2}$	500
Ethylene	$8.5x10^1$	$3.6x10^2$	9.3
Ethylene Dichloride	$2.9x10^1$	$4x10^{-2}$	343
Lindane	$1.3x10^3$	$1.3x10^{-4}$	$2.4x10^6$
Methyl Bromide	$2.2x10^1$	1.5	17
Napthalene	$1.3x10^3$	$5x10^{-2}$	$6.2x10^3$
Nitrobenzene	$7.1x10^1$	$1x10^{-3}$	$1.7x10^4$
N-Octane	$6.8x10^3$	$1.4x10^2$	21
Phenol	$2.7x10^1$	$7x10^{-6}$	$9.2x10^5$
Trifluralin	$7.3x10^3$	$6.7x10^{-3}$	$2.6x10^5$
Trichloroethylene	$9.8x10^1$	$4.4x10^{-1}$	77
Toluene	$1.4x10^2$	$3x10^{-1}$	143
1,1,1-Trichloroethane	$1x10^2$	1.5	29
Vinyl Chloride	$4x10^2$	$9.7x10^1$	10

characteristic final value under certain circumstances (e.g., stationary source of vapor, time independent biological and chemical reactions, reasonably constant moisture status over time). A hypothetical but plausible case of interest to examine is the steady-state distribution of gas concentration above a source of saturated vapor at the ground-water interface. It will also be assumed that the chemical undergoes a first order decay process characterized by a decay constant μ.

For this case, as shown in the Appendix, the steady-state gas concentration profile as a function of depth is given by:

$$C_v(Z) = C_v \frac{\text{Sinh }(qZ)}{\text{Sinh }(qL)} \qquad (14)$$

where

$$q = \left(\frac{\mu}{D_E}\right)^{1/2} = \left[\frac{\mu}{K_H D_v} (\rho_b K_d + \theta + \alpha K_H)\right]^{1/2} \qquad (15)$$

D_v is the soil gas diffusion coefficient, and L is the depth to ground-water. Profiles of concentration for various values of $Q = qL$ are given in Figure 3.9. Those curves with large Q represent compounds whose diffusion time through the soil is comparable to, or larger than, the half-life of the chemical. Hence, the vapor concentrations drop to low values in the soil.

Vapor Monitoring as a Detection Method

From the preceding discussion, several chemical characteristics may be identified which indicate whether a contaminant plume will be accompanied by a measurable vapor concentration. First, the chemical must have a non-negligible vapor pressure and density as part of the total concentration. Thus, compounds with very low values of Henry's constant K_H or compounds which adsorb strongly (large K_d) will be unlikely to have a large vapor density in soil. Second, the compound must be sufficiently mobile in the vapor phase to allow vapor to migrate significantly beyond the spill boundaries. The diffusion travel times, given in Table 3.5, are useful in determining whether this criteria will be met. Ultimately, the same conditions which limit vapor density (small K_H, large K_{oc}) will cause large diffusion travel times.

Finally, the compound must be persistent enough to travel beyond the spill boundaries without degrading into a form which is not detectable. Depending on the relation between the diffusion travel time and the compound half life, the vapor profile will drop off gradually or sharply between the spill and the soil surface, as in Figure 3.9.

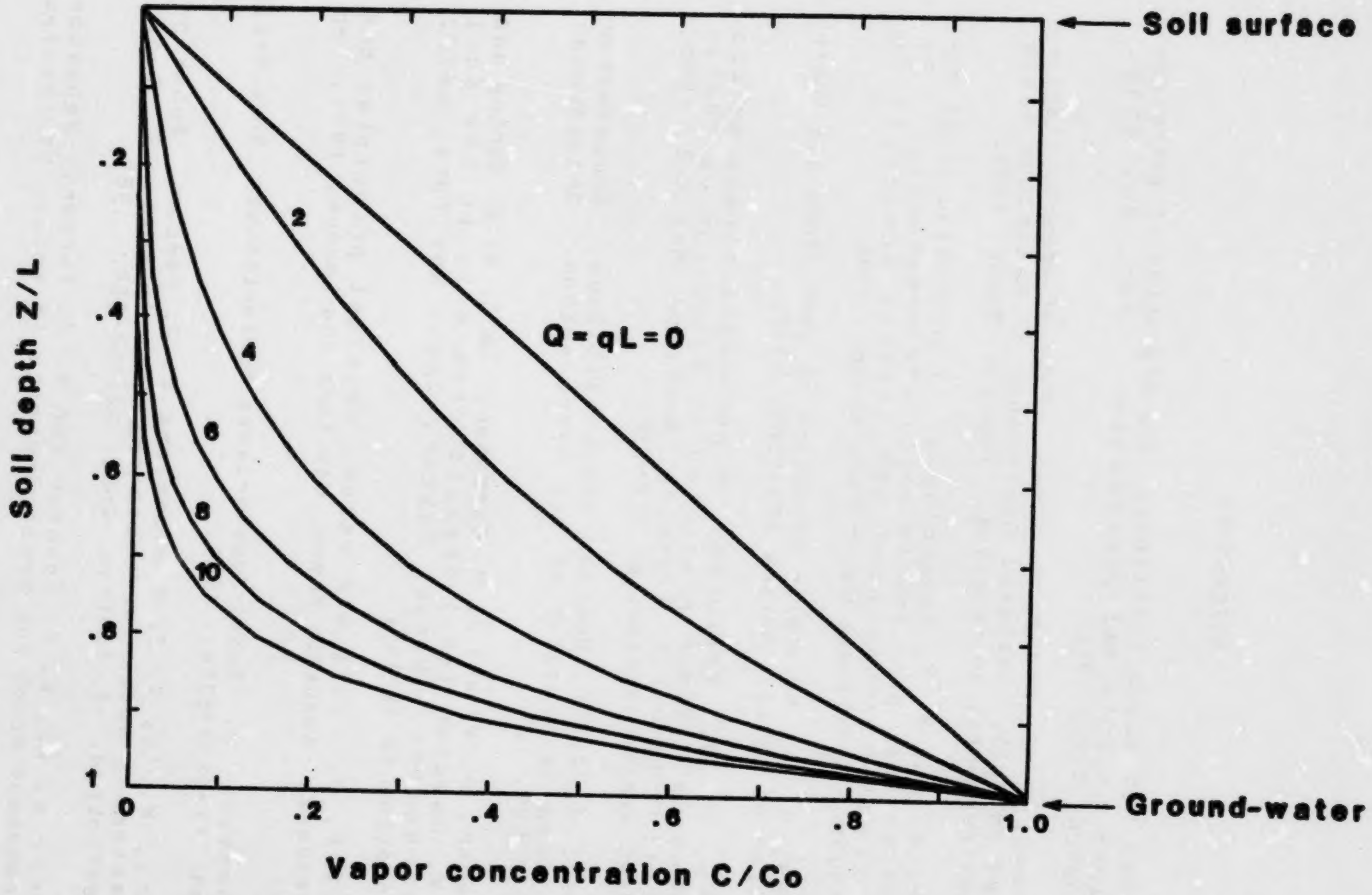


Figure 3.9. Steady state vapor concentration profiles between groundwater and the soil surface, for a compound undergoing first order degradation. Dimensionless parameter Q=qL is given by eq 15.

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APPENDIX

MATHEMATICAL THEORY OF DISSOLVED ORGANIC CHEMICAL TRANSPORT THROUGH SOIL

When a chemical which is present as a dissolved constituent of soil solution is also adsorbed to solid soil material and has a non-negligible vapor pressure, the total concentration C_T ($\mu g\ cm^{-3}$) of the chemical in units of mass per volume of soil may be written as

$$C_T = \rho_b C_a + \theta C_\ell + a C_v \tag{A.1}$$

where

C_a ($\mu g\ g^{-1}$) is the mass adsorbed per mass of soil
C_ℓ ($\mu g\ cm^{-3}$) is the mass dissolved per volume of solution
C_v ($\mu g\ cm^{-3}$) is the mass in vapor per volume of soil air
ρ_b ($g\ cm^{-3}$) is soil dry bulk density
θ ($cm^3\ cm^{-3}$) is soil volumetric water content
a ($cm^3\ cm^{-3}$) is soil volumetric air content

Conservation of Mass

The equation which represents conservation of mass for the chemical, called a continuity equation, may be written as (for one-dimensional flow)

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_{s\ell}}{\partial z} + \frac{\partial J_{sv}}{\partial z} + r = 0 \tag{A.2}$$

(Jury, et al., 1983)

where $J_{s\ell}$ ($\mu g\ cm^{-2}\ d^{-1}$) is the flux of dissolved chemical
J_{sv} ($\mu g\ cm^{-2}\ d^{-1}$) is the flux of chemical vapor

and r ($\mu g\ cm^{-3}\ d^{-1}$) is a general reaction term representing the net rate of transformation of chemical to another form.

Flux Equations

The one-dimensional flux of dissolved chemical through porous media is customarily written

$$J_{S_\ell} = - D_\ell \frac{\partial C_\ell}{\partial z} + J_W C_\ell \tag{A.3}$$

where J_w (cm d^{-1}) is the volume of solution and D_l (cm^{2}d^{-1}) is a combined diffusion-dispersion term representing the spreading of chemical by molecular collisions within solution and by moving around soil solid obstacles. In the field, dispersion is usually more important than diffusion.

The one-dimensional flux of chemical vapor through soil, called Fick's Law, is usually written as

$$J_{SV} = -D_V \, \partial C_V / \partial z \tag{A.4}$$

where D_V (cm^{2}d^{-1}) is the soil gaseous diffusion coefficient. A commonly used model for D_V is the Millington-Quirk model

$$D_V = \frac{a^{10/3}}{\phi^2} D_V^{air} \tag{A.5}$$

where D_V^{air} (cm^{2}d^{-1}) is the gaseous diffusion coefficient of the chemical in free air, and ϕ is soil porosity. Jury, et al. (1983), concluded that the value D^{air} = 4300 (cm^{2}d^{-1}) satisfactorily described intermediate molecular weight compounds.

Phase Relations

It is common to use simple equilibrium models to describe relationships among C_V, C_ℓ, and C_a in a three phase soil-water-air system. The simplest model to describe adsorption is the linear model.

$$C_a = K_d C_\ell \tag{A.6}$$

where K_d (cm^{3}g^{-1}) is called a distribution coefficient. This linear relationship has been shown to give good agreement with data for chemicals at dilute concentrations (Karickhoff, 1981). At higher concentrations a nonlinear Freundlich model

$$C_a = K_F C_\ell^{1/N} \tag{A.7}$$

where K_F and N are constants is frequently better than the linear model at describing data (Rao and Davidson, 1980).

Because K_d is soil-specific and because organic chemicals predominantly adsorb to soil organic matter, a modified distribution coefficient per unit organic carbon fraction is also used to describe the chemical adsorption affinity

$$K_{OC} = K_d/f_{OC} \tag{A.8}$$

where K_{OC} (cm^3g^{-1}) is an organic carbon distribution coefficient and f_{OC} is the soil organic carbon fraction. In cases where only the organic matter content f_{OM} is known, one may convert approximately to organic carbon fraction f_{OC} by using the equation

$$f_{OC} = f_{OM}/1.73 \tag{A.9}$$

Values of K_{OC} vary less than K_d between soils for a given chemical (Hamaker and Thompson, 1972). Thus, K_{OC} is a preferable benchmark property to use to represent the adsorption potential of a given compound.

The equilibrium relationship between C_V and C_ℓ is called Henry's Law

$$C_V = K_H C_\ell \tag{A.10}$$

where K_H (dimensionless) is called Henry's constant. Since this linear relationship commonly persists to saturation, K_H is usually calculated as the ratio of saturated vapor density and water solubility.

Partition Coefficients

It is useful to express direct relationships between the total concentration and the concentration in each phase. This is accomplished by combining the concentration relation (A.1) with the equilibrium relations (A.6) and (A.10). Thus, for the dissolved phase

$$\begin{aligned} C_T &= \rho_b K_d C_\ell + \theta C_\ell + a K_H C_\ell \\ &= (\rho_b K_d + \theta + a K_H)\, C_\ell \equiv R_\ell C_\ell \end{aligned} \tag{A.11}$$

where

$$R_\ell = \rho_b K_d + \theta + a K_H \tag{A.12}$$

is called the liquid partition coefficient (Jury, et al., 1983). In practice, the third term aK_H may be neglected in most cases. In addition, for strongly adsorbed chemicals (large K_d), only the first term p_bK_d is nonnegligible. For the vapor phase,

$$\begin{aligned} C_T &= p_bK_dC_V/K_H + K_HC_V + aC_V \\ &\quad (p_bK_d/K_H + \theta/K_H + a)C_V = R_VC_V \end{aligned} \tag{A.13}$$

where

$$R_V = p_bK_d/K_H + \theta/K_H + a \tag{A.14}$$

is the vapor partition coefficient. For strongly adsorbing chemicals, only the first term p_bK_d/K_H is nonnegligible.

The general transport equations above may be combined by plugging the flux equation expressions (A.3)-(A.4) into the continuity equation (A.2) and by expressing all concentrations in terms of the total concentration C_T when the partition coefficient definitions (A.12) and (A.14) are used. This results in the equation (assuming uniform soil properties)

$$\frac{\partial C_T}{\partial t} + r = D_E \frac{\partial^2 C_T}{\partial Z^2} - V_E \frac{\partial C_T}{\partial Z} \tag{A.15}$$

where

$$V_E = J_W/R_\ell = J_W/(p_bK_d + \theta) \tag{A.16}$$

is the effective chemical convective velocity, and

$$D_E = \frac{D_\ell}{R_\ell} + \frac{D_V}{R_V} \tag{A.17}$$

is the effective diffusion-dispersion coefficient. For volatile organic chemicals which have a high vapor density, the second term in e.g. A.17 dominates the first if the soil air content is high and if the water carrying the dissolved chemical is not moving rapidly through the soil. Thus, in this case,

$$D_E = \frac{D_V}{R_V} \tag{A.18}$$

Conversely, if the chemical has a low vapor density or if the air phase is negligible (i.e., ground water flow), then the first term dominates the second term and

$$D_E = D_\ell / R_\ell \tag{A.19}$$

Degradation Rates

The combined processes of biological and chemical degradation of organic chemicals are extremely complex, and can depend on a variety of factors such as temperature, organic matter content, water content, and microbial population density. Thus, the specific form of the reaction term r is often difficult to identify in a given situation. For this reason, simple idealized forms are often used to give approximate estimates. The most common form is the first order degradation model

$$r = \mu C_T \tag{A.20}$$

where μ (d^{-1}) is a first order degradation rate coefficient. It is related to the effective half life $T_{1/2}$ (d) of the compound by the equation

$$T_{1/2} = 0.693/\mu \tag{A.21}$$

Steady State Profiles

If the compound is present at saturation level in ground water and diffuses upward while undergoing first order decay, the profile will eventually reach a steady state value whose shape is described by the steady state form of Eq. (A.15) with $V_E = 0$ and $r = \mu C_T$, or

$$D_E \frac{d^2 C_T}{dz^2} = \mu C_T \tag{A.22}$$

with $C(L) = C_0$ and $C(0) = 0$.

The solution to this equation may be written as

$$C(z) = C_0 \frac{\sinh(qZ)}{\sinh(qL)} \tag{A.23}$$

where

$$q = (\mu/D_E)^{1/2} \tag{A.24}$$

CHAPTER 4

MEASUREMENT METHODOLOGIES

The following sections discuss sampling and analytical methodologies for monitoring volatile organics in the subsurface. The sections are: Sampling Methods, Sampling Design, Quality Assurance, and Analytical Methods.

SAMPLING METHODS

This section presents various sampling methodologies used to monitor subsurface contamination. These methods include: headspace measurements, ground probes, flux chamber measurements, and sampling with sorbents (usually passive sampling).

The techniques identified are capable of providing a yes or no answer to whether subsurface hydrocarbon contamination is present. However, the techniques do not all provide an equivalent measurement. The ground probe and headspace measurement techniques measure a soil gas concentration, the flux chamber technique measures an emission rate, and the passive sampling technique measures some function of an average soil gas concentration. The technique(s) selected for a particular application will be dependent on the objectives of that study.

All the techniques can be divided into two steps, sample collection and analysis. Analytical instrumentation for hydrocarbon analysis is commercially available but is relatively complex and expensive. The sample collection equipment discussed is not generally commercially available, but is usually simple to construct and operate, however some of the equipment described is protected by patent.

Various techniques have been successfully used for ground-water contamination investigations at a variety of sites. However, the techniques discussed below are not standard methods and have not yet been adequately evaluated. Therefore, best results will be obtained when the techniques are used by experienced investigators who are familiar with the methods used and the local geology and hydrology. All the techniques are dependent on the movement of volatilized organic species up through the overlying soil. Any limitations of this transport will limit the utility of these techniques. The suitability of each technique for various types of site conditions is discussed and compared in this section.

Headspace Measurements

This section discusses the determination of hydrocarbon concentrations by analyzing the headspace gas from samples collected in a dry well or from soil cores.

Headspace Measurements in Dry Wells--

Sampling the headspace in existing subsurface structures is a simple technique that can yield valuable preliminary information. The technique involves collecting grab samples or using a portable hydrocarbon analyzer to measure the headspace concentration in monitoring wells, storm sewers, utility vaults, or other subsurface structures. The results obtained provide information regarding the composition and extent of any contaminant plume and assist in developing an optimal sampling strategy for subsequent investigative work.

Recommended use--It is recommended that headspace measurements be made at existing subsurface structures as the first phase of any subsurface contamination investigation. The technique is quick, simple, and economical. Furthermore, it can save substantial amounts of time and money by providing input data for selection of an appropriate sampling strategy.

Technique applications--Headspace sampling is typically employed as part of any Remedial Investigation/Feasibility Study (RIFS). One example is given below.

A tanker truck spill caused 5,500 gallons of jet fuel to contaminate an area of high ground-water. A preliminary study installed ground-water monitoring wells along two perpendicular lines. A subsequent study was under taken to develop sampling methods and to define the contaminant plume (Radian Corporation, 1984). The first stage of sampling involved removing the well caps and collecting headspace samples in gas syringes for on-site gas chromatograph/flame ionization detector (GC/FID) analysis. Additional measurements were made by using a portable total hydrocarbon analyzer. The results of the headspace analyses indicated that the plume had increased in area since the initial study. Therefore, the gridded sampling area was expanded accordingly, prior to an intensive, follow-up investigation.

Limitations--The limitations associated with this sampling technique include:

- interferences (e.g., methane in sewers);

- subsurface structures or wells are not always present at investigation sites (or not optimally located);

- volatile hydrocarbon species can diffuse out of unsealed subsurface structures; and

- negative test results are inconclusive, i.e., the absence of hydrocarbons in the headspace of a subsurface structure does not guarantee that hydrocarbons are not present in the surrounding soil.

Headspace Measurements of Soil Cores--
The headspace gas or extracted solids of a soil core can be analyzed to determine hydrocarbon concentrations. To obtain a sample, a technique known as grab sampling can be used. An "undisturbed" soil core is collected by using an auger or by driving a tube into the ground and is then sealed in a sample container. Using this technique, liquid as well as gaseous hydrocarbon contamination can be detected directly. Two approaches can be taken. First, the sample container can be half filled with soil. Hydrocarbons can then volatilize into the vacant headspace. Care should be taken to ensure headspace and soil without providing any headspace. Soil gas is then extracted directly from soil pores.

Recommended use--This method of measuring hydrocarbons is recommended when the sampling crew has a modest level of technical expertise or when sophisticated sampling equipment is either not available or not cost-effective. The method works best when sampling sandy soils containing little organic matter.

The technique of grab-sampling of soil cores is typically both simple and quick to perform. Minimally, the method requires only one person, one hand auger, and sample storage containers. Analyses can be performed off site at a later date.

Technique applications--Grab sampling of soil cores can be accomplished using a variety of equipment as illustrated by the recent review from the U.S. EPA (1984). The review is summarized in Table 4.1. A number of researchers have applied this technique to detecting hydrocarbon soil gases at various subsurface levels. In most cases, shallow soil gasses were collected to assess very deep sources of vapors. Variety is evident in sampling depth, collection equipment, storage, and analytical methods.

TABLE 4.1. CRITERIA FOR SELECTING SOIL SAMPLING EQUIPMENT

Type of Sampler	Obtains Core Sample		Most Suitable Core Types			Operation in Stony Soils		Most Suitable Soil Moisture Conditions			Access to Sampling Sites During Poor Soil Conditions		Relative Sample Size		Labor Requirements	
	Yes	No	Clay	Sand	Inter	Fav	Unfav	Wet	Dry	Inter	Yes	No	Sm	Lg	Sngle	2/More
A. Hand Auger																
1. Screw-Type Augers	X				X		X	X			X		X		X	
2. Barrel Augers																
a. Post-Hole Auger	X		X			X		X			X			X	X	
b. Dutch Auger		X	X			X		X								
c. Regular Barrel Auger		X	X			X				X	X		X		X	
d. Sand Augers		X		X		X				X	X			X	X	
e. Mud Augers		X	X			X		X			X			X	X	
3. Tube-Type Samplers																
a. Soil Probes																
(1) Wet Tips	X				X		X	X			X					
(2) Dry Tips	X				X		X	X			X		X		X	X
b. Veihmeyer Tubes	X				X					X			X		X	
c. Thin-Walled Tube Samplers	X		X				X			X	X			X		X
d. Peat-Samplers	X		X				X	X			X			X		X
B. Power Auger																
1. Hand-Held Screw Type Power Auger		X			X	X				X	X			X		X
2. Truck Mounted Auger					X											
a. Screw Type		X			X	X		X				X		X		X
b. Drive Sampler	X		X			X				X		X		X		X
3. Tripod Mounted Drive Sampler	X		X							X		X		X		X

For example, Horvitz (1954) reported using a hand auger or drilling equipment to search for oil and gas. Samples were collected at 8 to 12 foot depths and brought to the surface. The samples were stored in glass jars or cans, and were later analyzed by using a vacuum analytical-combustion technique. In another study, Horvitz (1954) used a piston-type coring device to collect shallow soil samples during offshore oil and gas prospecting activities. For this study, samples were stored in plastic bags (with a reported shelf-life of several months), and then extracted samples were analyzed by using gas chromatography (GC). Horvitz noted that onshore samples need to be collected at a depth greater than 6 feet to ensure a quality sample whereas shallower depths were sufficient for offshore sample collection.

Devine and Sears (1977) collected and analyzed over 1,000 cores in a search for oil and gas deposits in Australia. Samples were collected by mechanically drilling to a 9 to 10-foot depth and then by inserting a coring device. Samples were stored in heat-sealed polyethylene bags. Sample preparation for analysis by GC included acid leaching and cryogenically trapping the hydrocarbons.

Smith and Ellis (1963) also collected soil cores (0-40 foot depth) in cans soldered to seal in the sample. For GC analysis, the headspace gas was removed from the cans through a hole in the top by using a glass syringe. They conducted studies concerning the effect of refrigerated versus non-refrigerated sample storage. Their results indicated that hydrocarbon concentrations decreased in samples stored at 68-95°F versus refrigerated samples stored at 32°F or pasteurized samples (exposed to 185°F for short periods). They also concluded that the organic content in soil samples may interfere with hydrocarbon detection from underlying oil and gas deposits. However, Horvitz (1972) refuted this conclusion when he reported that grass and roots contribute negligible amounts of saturated hydrocarbons to the soil atmosphere. In addition, Horvitz disagreed with the need for sample refrigeration by stating that minimal headspace above the sample was the key to a long shelf-life.

In other oil and gas exploration efforts, Pogorski and Quirt (1981) collected soil samples at a 2 foot depth by using hand or power augers. Instead of using plastic bags for storage, they used specially designed aluminum cans. The samples were sealed in the air-tight cans and later were analyzed by GC. Similar methodologies have been used by several oil and gas exploration companies (Eklund, 1985).

Limitations--The primary limitation of this technique is that it is better suited for measuring adsorbed organics rather than free organics in the interstitial pore spaces. Hanisch and McDevitt (1984) reported that any headspace present in the sample container will lead to desorption of organics from the soil particles. Unless the soil type, headspace volume, temperature, sample handling techniques, and storage time are held constant, relative concentration levels between soil samples are not comparable.

Another limitation to this technique is the possible loss of volatile hydrocarbons when the sample is removed from the ground or transferred for analysis. Sample exposure to the atmosphere has been successfully avoided by capping the soil core tubes. Bednas and Russell (1967) capped tubes with sealing wax and reported a shelf-life of at least 12 months. Their work involved detecting natural gas leaks by trenching to the desired sampling depth and by driving tubes (26 in x 2 in) into the trench walls. A carrier gas was used to flush soil gas from the samples to a GC analyzer. Hanisch and McDevitt (1984) reported a technique used at several hazardous waste sites. The core sampler used (see Figure 4.1) consists of a brass core sleeve which is pressed into the soil to a sufficient depth to fill the sampler but not so deep as to compress the sample. The method works best for clays and silts of medium moisture content. After excess soil is removed, the sleeve is sealed with a Teflon-lined cap. The samples are stored at room temperature. Headspace (i.e., pore space) gas collected by a syringe through a port are analyzed by GC.

In addition to loss of volatile hydrocarbons, degradation of organic compounds may also occur because of time delay between collection and analysis. This collection method is not appropriate for rocky soils nor is it well suited for loose sandy soils that may not be adequately held in the tube sampler. Sample retaining rings can be used with some samplers to retain coarse samples.

Driven Probes

For the driven ground-probe technique, a drive tip is attached to a ground probe which is then forced into the ground. This minimizes disturbance of the sampling environment. Openings in the tube near the leading edge allow soil gases to enter the tube. Sample gas is extracted from a port at the upper end of the tube using a gas-tight syringe. Analysis is performed by using GC.

An improvement to the ground-probe technique is to minimize the internal volume of the sampler. This means a smaller sample volume is necessary to purge the system, and, consequently, a more representative sample is obtained.

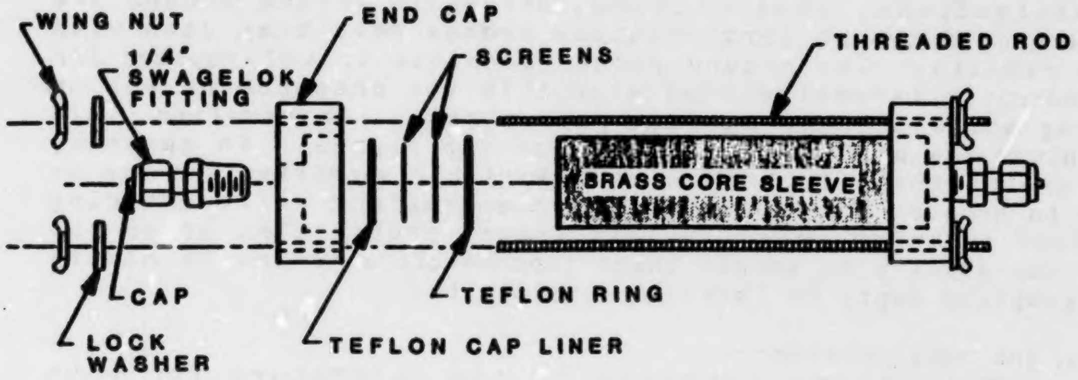

WING NUT
1/4" SWAGELOK FITTING
END CAP
SCREENS
THREADED ROD
BRASS CORE SLEEVE
CAP
LOCK WASHER
TEFLON RING
TEFLON CAP LINER

Figure 4.1. Soil core sample sleeve (Hanisch and McDevitt, 1984).

Applications of small-volume, driven ground probes are presented in a later section.

Recommended Use--

The ground probe technique has been successfully used at a variety of sample sites. For ground-water contamination investigations, small-volume, driveable ground probes are preferred, although larger-volume probes have been used with good results. The ground-probe technique is well-suited for ground-water investigations except in the presence of wet or clayey soils or near surface rock strata. In addition, this technique has been accurately used to map plumes. In general, the ground-probe technique is relatively sensitive and can be used to measure subsurface gas concentrations while avoiding surface interferences. Driven ground probes also offer the user the ability to sample below impermeable soil and to modify the sampling depth to increase sensitivity.

Technique Applications--

Applications reported in the literature for both large-volume ground probes and small-volume ground probes are presented in this section. The internal volume of the ground probe significantly affects the measurement process and the utility of the resulting data. The small internal volume ground probes can be used to attempt to measure the "true" soil-gas concentration. The small volume permits the air inside the probe to be purged and a small (e.g., 1 mL) sample to be collected without substantially altering the equilibrium of the soil-gas concentration. Alternatively, the use of large internal volume ground-probe typically involves sampling several liters of soil gas. This sampling may not permit a "representative" soil-gas sample to be collected under most conditions but allows for the soil gas to be concentrated prior to analysis or multiple aliquots to be extracted. The large-volume ground probes are typically used for investigations that seek to determine relative soil gas concentrations or that are concerned with whether or not contamination affects a given area.

Large-Volume Ground Probes--

Ground probes have been widely used. For example, Russell and Appleyard (1915) used a 2 foot long probe (shown in Figure 4.2) which was hammered into the soil to the desired depth, and then the inner rod was pushed down another 1/4 in. Neglie and Favretto (1962) used a similar design (see Figure 4.3) and procedure except that the outer tube was raised 0.7 to 1.0 foot after placement to provide a pathway for soil gas to enter the sample. They detected maximum hydrocarbon concentrations in the soil gas immediately after inserting the probe. However, Neglie and Favretto concluded that grab sampling of soil cores provided better results than their

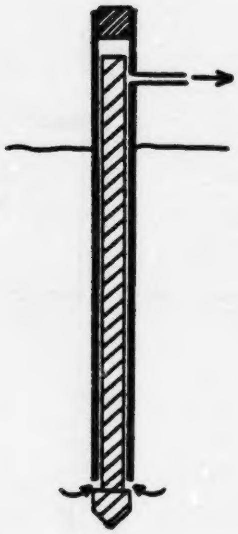


Figure 4.2. Ground-probe design used by Russell and Appleyard (1915).

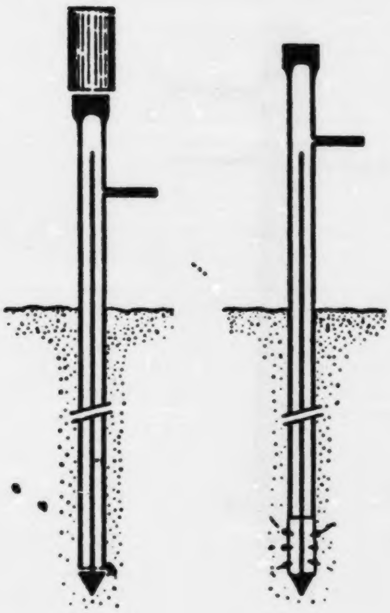


Figure 4.3. Ground-probe design used by Neglia and Favretto (1962).

technique. Tackett (1968) used a probe with a slightly different design to avoid plugging the sampling port during insertion. A slot was cut in the side near the tip to allow soil gas to be pulled into the probe (see Figure 4.4). DeCamargo (1974) modified Tackett's design so that samples could be collected in glass ampules which could then be sealed and stored for later analysis.

Other researchers have used driven probes with perforated ends to measure landfill gases (Thorburn, et al., 1979; Colenutt, et al., 1980), carbon dioxide and oxygen (Lovell, et al., 1980) and to detect hydrocarbon spills (Spittler, et al., 1985). For example, Thorburn, et al. (1979), sampled landfill gases by using a probe in which a pointed rod was placed inside the tube during probe insertion and was then removed before sampling (see Figure 4.5).

Tracer Research Corporation (TRC) has used hollow, perforated metal probes for a number of site investigations with potentially contaminated ground-water (Lapalla, et al., 1984; Marrin, et al., 1984). For depths of less than 10 feet, probes are driven to the desired sampling depths. For depths greater than 10 feet, the probe is driven ahead of the bottom of a hollow stem auger that has been advanced to just above the desired depth. Soil gas is pumped from the sampling location at a rate of 0.5 to 0.8 gal/min for several minutes. Then a syringe is used to collect samples for GC analysis. Others (Lovell, et al., 1980; Walther, et al., 1983) have reported use of this method.

Tracer Research Corporation (Lapalla, et al., 1984, Marrin, et al., 1984) has documented sampling results from over 12 sites with varying site conditions such as ground-water depth of 10 to 125 feet, varying clay and moisture levels in the soil, and different organic contaminants present. Tracer Corporation found that this technique detected organic compounds in almost all situations, even above one site with a 30 foot caliche layer overlying the ground-water table. The technique could be used to map known plumes accurately ; however, it is not suitable for wet, clayey soils or where an uncontaminated aquifer overlies one that is polluted. Sampling results from the soil gas and the polluted ground-water correlated well even with repeat samples on successive days. TRC (Lapalla, et al., 1984; Marrin, et al., 1984) has reported that gasoline vapors in soil act differently than chlorinated organic vapors. Marrin (1985) reports that the TRC ground probes can be used to map gasoline plumes at sites where the water table is relatively shallow or where probes can be driven below the oxidation zone in soils. Petroleum hydrocarbons are often absent from the shallow soil gas overlying gasoline-polluted ground-water; this is believed to be due to

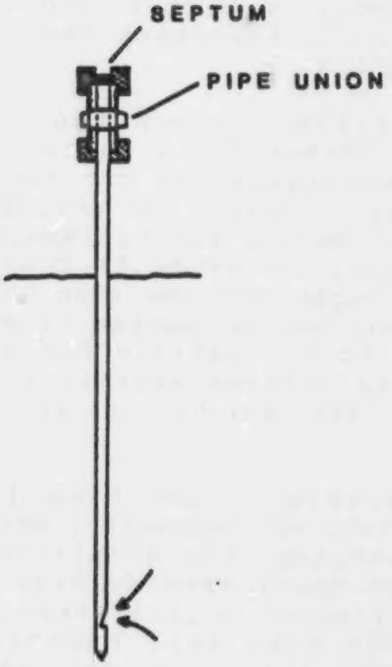

SEPTUM
PIPE UNION

Figure 4.4. Ground-probe design used by Tackkett (1968).

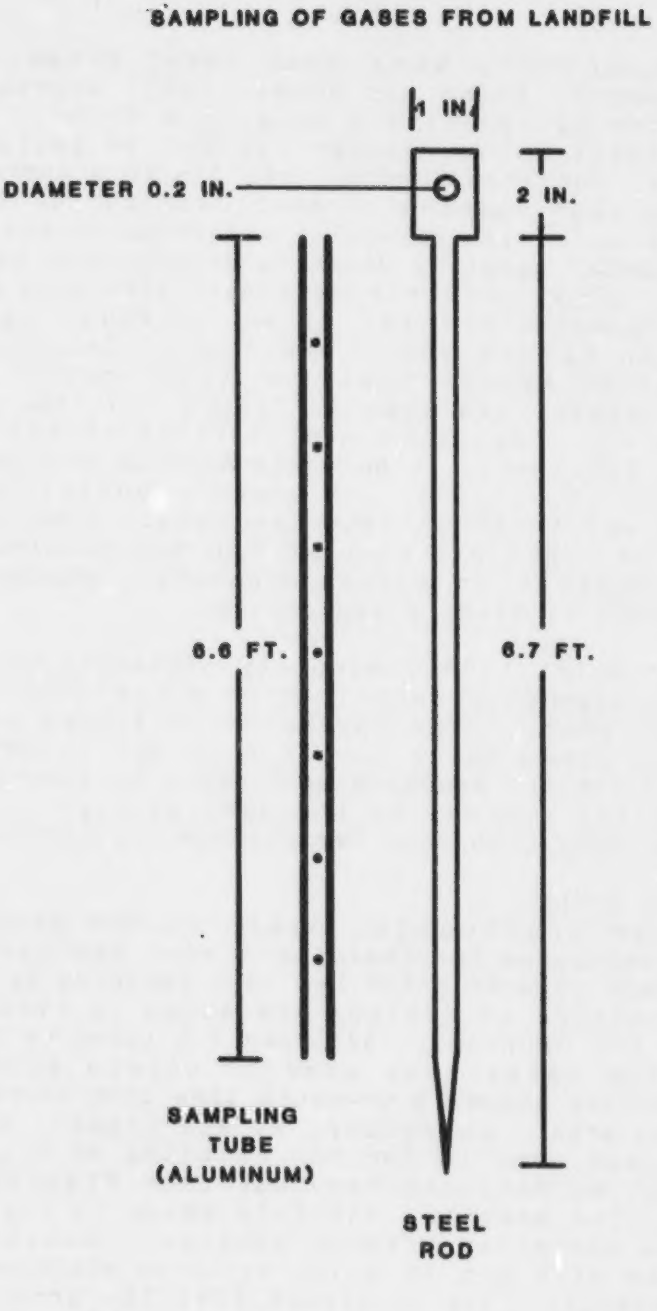

SAMPLING OF GASES FROM LANDFILL
1 IN.
DIAMETER 0.2 IN.
2 IN.
6.6 FT.
6.7 FT.
SAMPLING TUBE (ALUMINUM)
STEEL ROD

Figure 4.5. Ground-probe design used by Thorburn, et al.(1979).

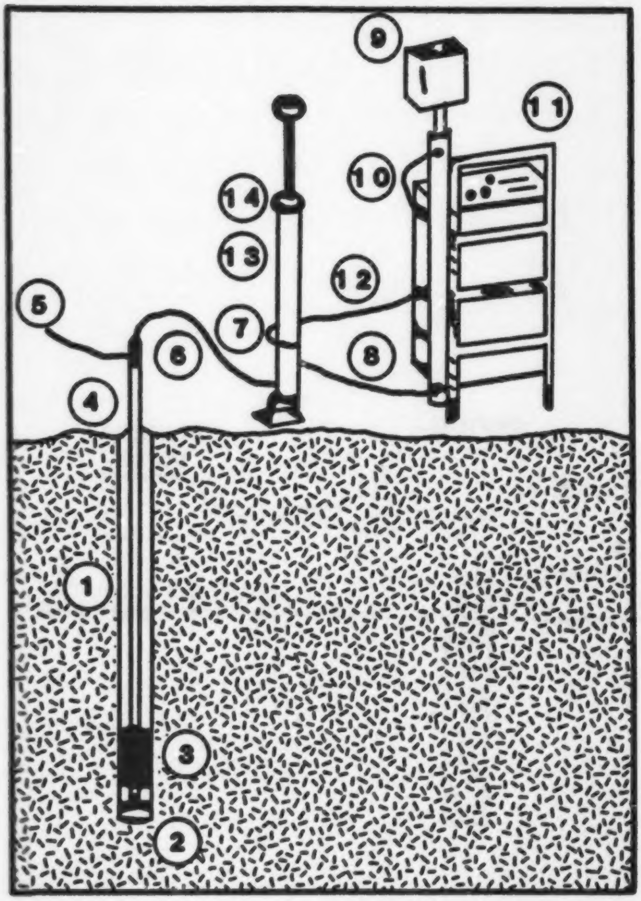
biodegradation of the gasoline vapors in the near-surface soil layers.

Several researchers have used novel ground-probe variations. For example, Jones and Drozd (1983) searched for oil and gas deposits by augering a hole to a 13 foot depth, inserting an inflatable rubber packer (probe) to isolate the bottom of the hole, and then pumping soil gas to a portable GC for analysis. They also sampled at shallower depths (1 to 2 feet) and detected more high molecular weight compounds. They reported that the deeper sampling depths provided more reliable results (Schmidt, 1985). Other researchers have used similar techniques. For example, Lovell, et al. (1980), used the equipment shown in Figure 4.6. Swallow's (Eklund, 1985) technique was similar except that the void volume of the sampler was much larger. As seen in Figure 4.7, the sampler was a plugged corehole. Spittler and Clifford (1985) used a method similar to Swallow's. A hole was augered to a depth of 12-18 in. The hole was capped, and a probe constructed of plumbing fittings was inserted into the hole. Approximately 0.0035 ft ^{3}/min of soil gas was removed for 4.6 minutes until the soil-gas concentration became constant. Analysis was performed in the field by using a portable GC.

Pogorski and Quirt (1981) manually collected helium gas samples by using an apparatus described as a low-dead-volume, nonclogging steel probe. The apparatus is a type of auger which allows sample gases to be pumped from the bottom. Van Bavel (1965) has described sampling soil gases by inserting the needle of the sampling syringe to the desired depth. Though exceedingly simple, this technique has obvious limitations.

Small-Volume Ground Probes--

As mentioned previously, small-volume probes are believed to be advantageous in obtaining a more representative sample. Use of this type of probe has been reported by several researchers. Variations in designs are shown in Figures 4.8 (used by Swallow and Gachwend, 1983) and 4.9 (used by Walther, et al., 1983). The latter was used to obtain measurable benzene concentrations across a transect line that corresponded to a plume of known area. LaBrecque, et al. (1984), modified Walther's design and used it for the sampling of a gasoline spill at Death Valley National Monument (see Figures 4.10, 4.11, and 4.12). The sampling manifold shown in Figure 4.12 was shown to give carryover between samples. Sample entry holes were covered with 8 x 10-4 in. sintered stainless steel disks to avoid blockage. They concluded that the ground probe technique provided better results than geophysical methods used to define the dimensions of the plume but the ground probes were prone to false positive readings. A similar design was used by Kerfoot, et al. (1986), to investigate a site



Equipment for determination of mercury and radon in soil air as used at Cachinal, N. Chile. (1) 100 mm dia. 3-4 m deep auger drill hole (2) loose soil (3) rubber packer (4) 25 mm dia. Dural prope (5) packer pressure line (6) PTFE 5 mm dia. line (7) dust filter (8) line to radon monitor (9) radon monitor (10) line to mercury spectrometer (11) mercury spectrometer (12) line to pump (13) 1 l. pump (14) outlet.

Figure 4.6. Ground-probe design of Lovell, et al. (1983).

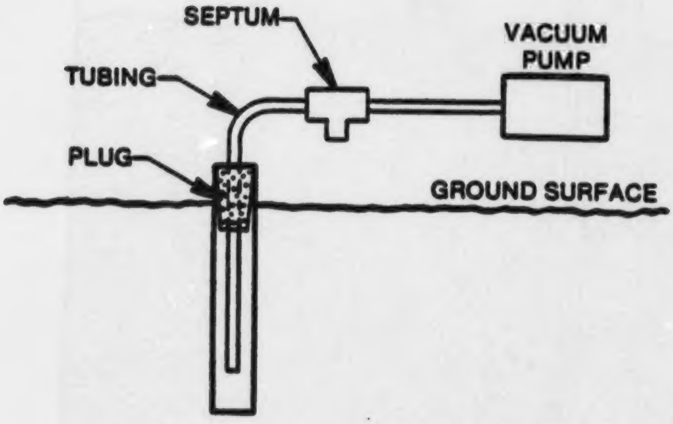

SEPTUM
VACUUM PUMP
TUBING
PLUG
GROUND SURFACE

Figure 4.7. Ground-probe design used by Swallow and Gschwend, 1983.

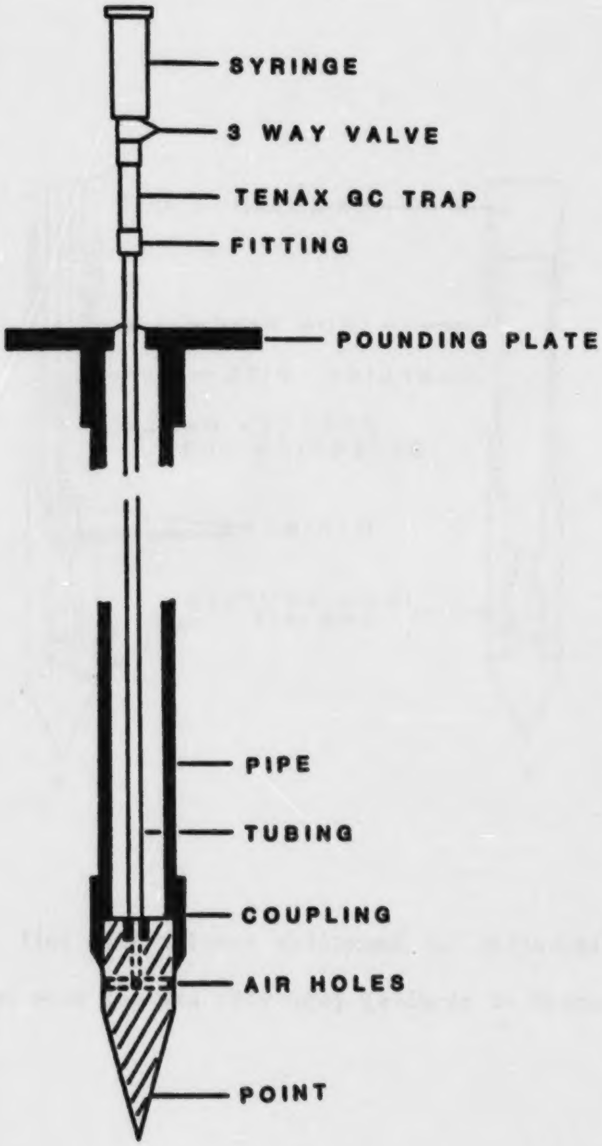
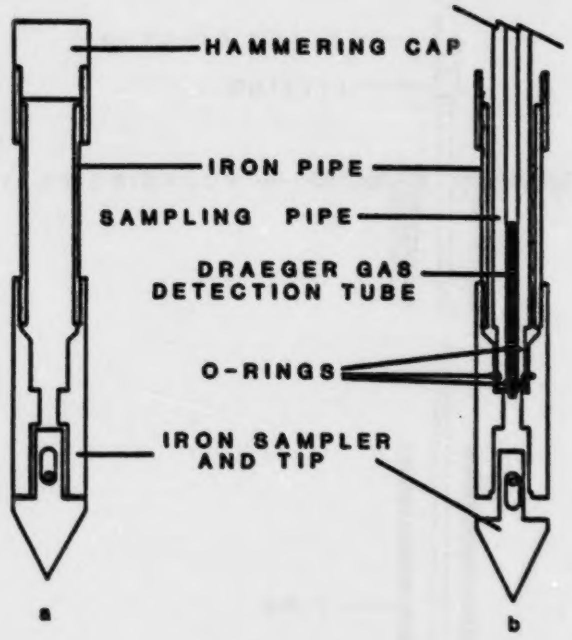

SYRINGE
3 WAY VALVE
TENAX GC TRAP
FITTING
POUNDING PLATE
PIPE
TUBING
COUPLING
AIR HOLES
POINT

Figure 4.8. Ground-probe design used by Swallow and Gschwend (1983).


HAMMERING CAP
IRON PIPE
SAMPLING PIPE
DRAEGER GAS DETECTION TUBE
O-RINGS
IRON SAMPLER AND TIP
a
b

a - Configuration for hammering sampler into soil

b - Placement of sampling pipe with Draeger tube into the sampler

Figure 4.9. Ground-probe design used by Walther, et al. (1983).

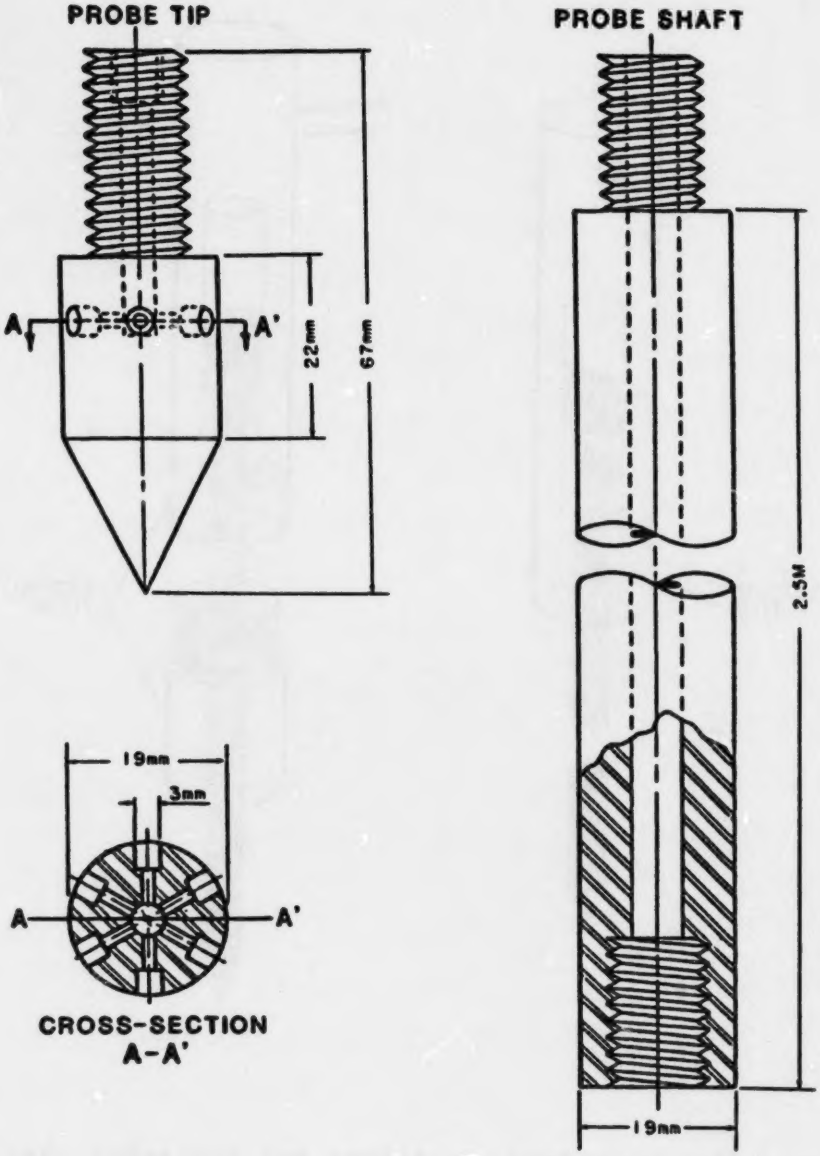

PROBE TIP
PROBE SHAFT
A
A'
22mm
67mm
2.5M
19mm
3mm
A
A'
CROSS-SECTION
A-A'
19mm

Figure 4.10. Ground-probe design used by LaBrecque, et al. (1984).

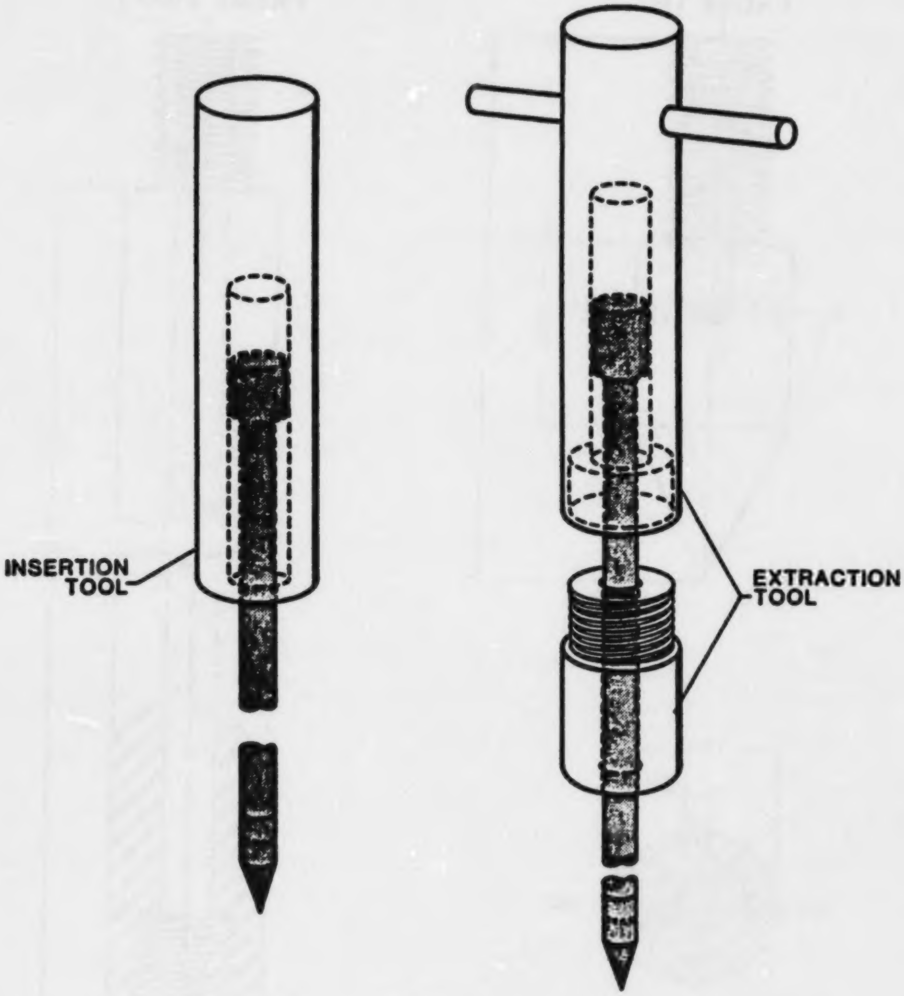

INSERTION TOOL
EXTRACTION TOOL

Figure 4.11. Ground-probe driver and extractor used by LaBrecque, et al. 1984).

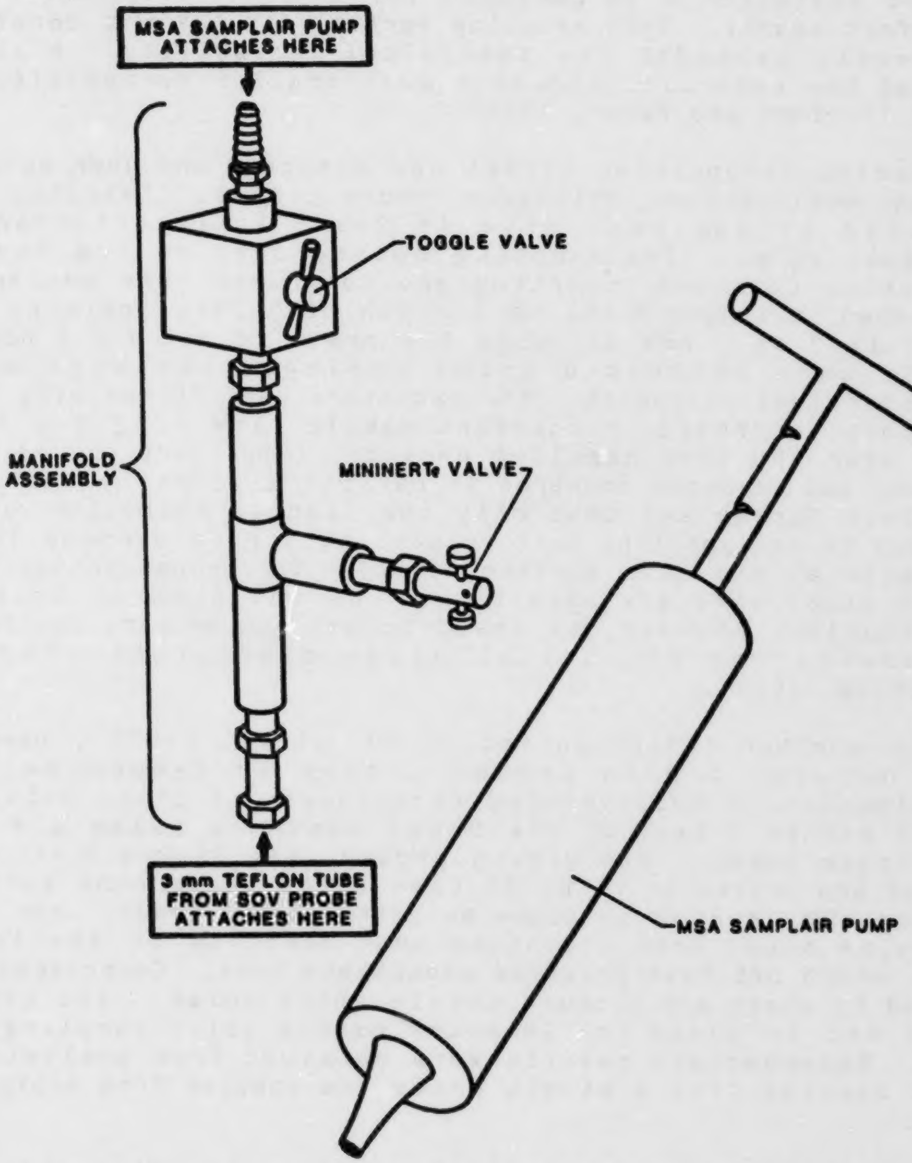

MSA SAMPLAIR PUMP ATTACHES HERE
TOGGLE VALVE
MANIFOLD ASSEMBLY
MININERT® VALVE
3 mm TEFLON TUBE FROM SOV PROBE ATTACHES HERE
MSA SAMPLAIR PUMP

Figure 4.12. Sampling manifold and pump used by LaBrecque, et al. (1984).

contaminated with halogenated organic compounds. They found that the soil gas concentration varied significantly (relative standard deviation = 42 percent) for adjacent locations (less than 7 feet apart). This sampling variability was not constant and greatly exceeded the analytical variability. A later survey at the same site showed a much smaller variability of 12% rsd (Kerfoot and Mayer, 1986).

Radian Corporation (1984) has designed and used several different small-volume, driveable ground probes. Sampling was conducted at the same site in Death Valley studied by LaBrecque, et al. The sampling method used by the Radian Corporation involved inserting ground probes (the design is illustrated in Figure 4.13) to a depth of 3 feet, raising the outer tube 2 in., and allowing the probe to sit for 2 hours. Samples were collected using syringes and evacuated stainless-steel canisters. The canisters were fitted with flow regulators to provide a constant sample flow of 3.5 x 10-4 ft/min over the 4-hr sampling period. [The study showed that the plume had advanced compared to earlier studies by the U.S. Geological Survey and that only the lighter molecular weight compounds in the gasoline were present at 1 ppbv-carbons level or greater at the near surface level.] The ground probes used in this study were adequate to define the general area of contamination; however, an insufficient number were available for demarcating the actual plume dimensions (Radian Corporation, 1984).

In another investigation, Crow, et al. (1985), used 32 small-volume, driven ground probes to determine the effectiveness of soil-venting techniques. A pilot hole was drilled within 2 feet of the final depth by using a 4 in. hollow-stem auger. The ground probes (see Figure 4.14) were inserted and driven to 16 to 22 feet below the ground surface and then were sealed in place by using cement grout. For this particular site, Crow indicated that sampling at shallower depths would not have provided acceptable data. Compressed air was used to clear any blocked sample entry holes. The ground probes sat in place for 24 hours before daily sampling was begun. Reproducible results were obtained from analysis of repeat samples from a single probe and samples from duplicate probes.

Limitations--The major limitations in using soil gas probes are that they are best suited for shallow sampling; they are not well suited for rocky or wet, clayey soils; and obtaining a representative sample is difficult. Other problems include: the method is labor intensive, sample parts may become occluded during probe insertion, and ambient air can in some cases migrate down the outside of the probe shaft and dilute the sample.

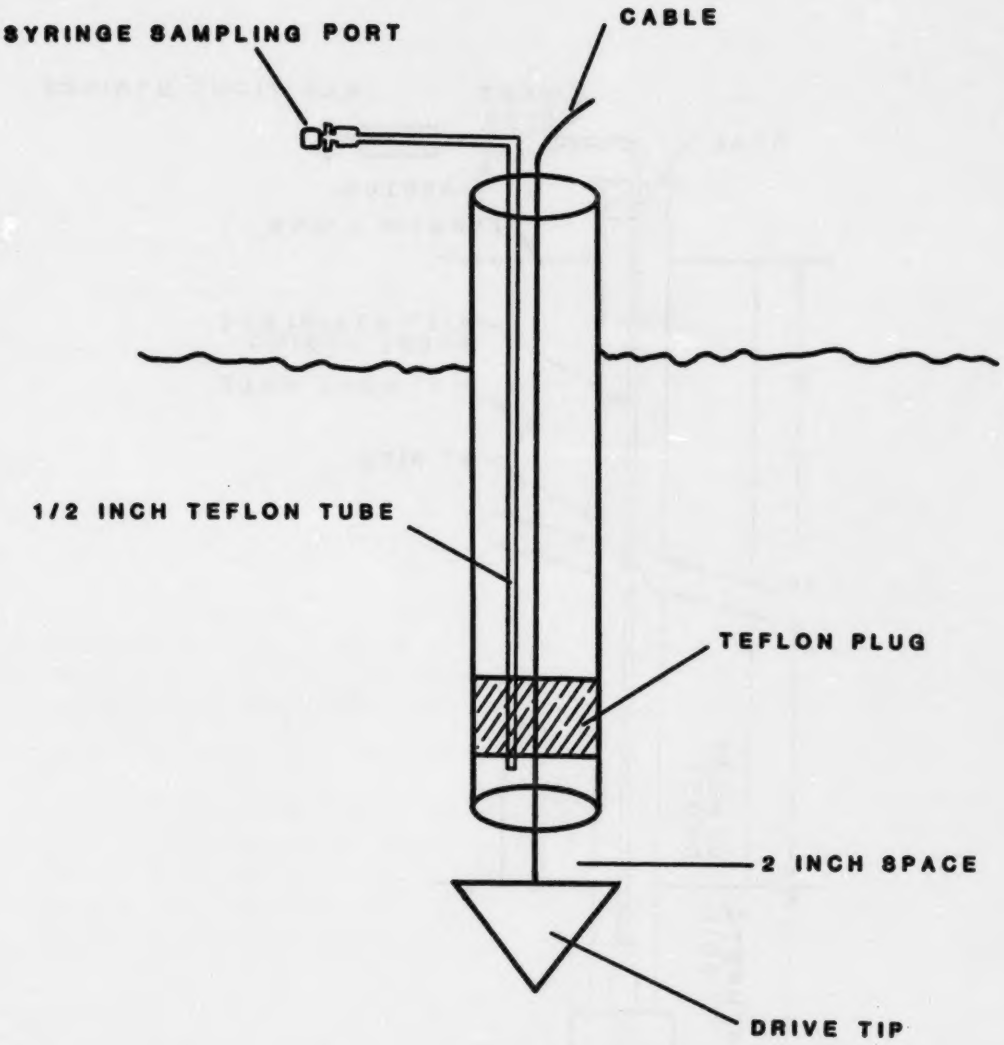

SYRINGE SAMPLING PORT
CABLE
1/2 INCH TEFLON TUBE
TEFLON PLUG
2 INCH SPACE
DRIVE TIP

Figure 4.13. Ground-probe design used by Radian Corporation (1984).

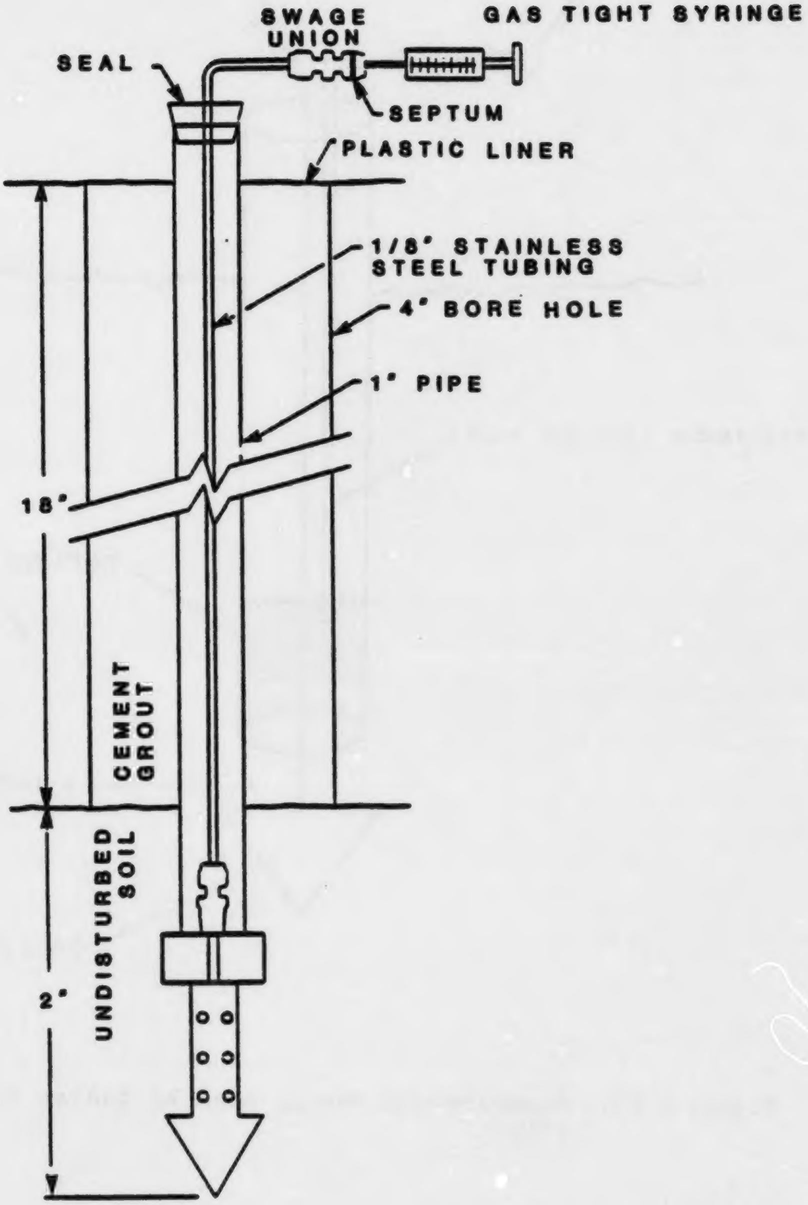

SWAGE UNION
GAS TIGHT SYRINGE
SEAL
SEPTUM
PLASTIC LINER
1/8" STAINLESS STEEL TUBING
4" BORE HOLE
1" PIPE
18"
CEMENT GROUT
UNDISTURBED SOIL
2"

Figure 4.14. Ground-probe design used by Crow, et al. (1985).

Surface Flux Chambers

The surface flux chamber technique involves the use of an enclosure device to sample gaseous emissions from a known surface area. Sweep air flows through the chamber. The exit gas is analyzed on-site or collected for later analysis. Knowledge of the flow rate of air through the chamber and of the concentration of the exit gas enables the emission rate to be calculated.

Recommended Use--

The surface flux chamber is particularly applicable to measuring population exposures since gaseous emissions are being measured at the surface level. However, surface hydrocarbon levels are generally lower than subsurface levels; therefore, the usefulness of the flux chamber method is limited where the soil-gas concentration is low. Best results are obtained when sophisticated sampling techniques (e.g., stainless steel evacuated canisters) and/or sensitive detection systems (e.g., GC) are used. The technique minimizes disturbance of the soil or of any associated emission processes. Sampling is quick (normally requires 1/2 hr per sampling point), requires simple equipment, and is suited to most soil types. Radian Corporation (Schmidt, et al., 1983) reported 88.5 percent to 124 percent recoveries when a 36-component organic standard was used and was introduced into the sampling system. In addition, a range of 2.3 x 10-11 to 1.1 x 10-4 $\mathrm{lb/ft^2/min}$ was determined (Radian Corporation, 1984; Schmidt, et al., 1982). The Radian Corporation (Balfour, et al., 1985) also reported accuracies of better than ±10 percent and analytical variabilities within ±20 percent determined by an independent audit.

Technique Applications--

In 1983, Eklund and Schmidt (1983) performed a review on the development of the flux chamber sampling technique. This review revealed only three groups of researchers using this method for measuring hydrocarbon emission rates. However, this method has long been used to measure fluxes of non-hydrocarbon gases. Sekulic and Delaney (1980) suggested the application of this method for measuring hydrocarbon emissions from a wastewater treatment lagoon. Their device consisted of a floating truck inner tube with translucent plastic covering one end. Sweep air was used to force a sample to a portable organic vapor analyzer (OVA) equipped with a FID. Another researcher, Zimmerman (1977), used a 2.4-foot diameter flux chamber with a collapsible top to measure biogenic hydrocarbon emissions. Analysis took place within 24 hours using three separate GCs to examine a broad range of hydrocarbon species. The flux chamber used by Schmidt (1983), consisted of a stainless steel/acrylic chamber (see Figure 4.15) with

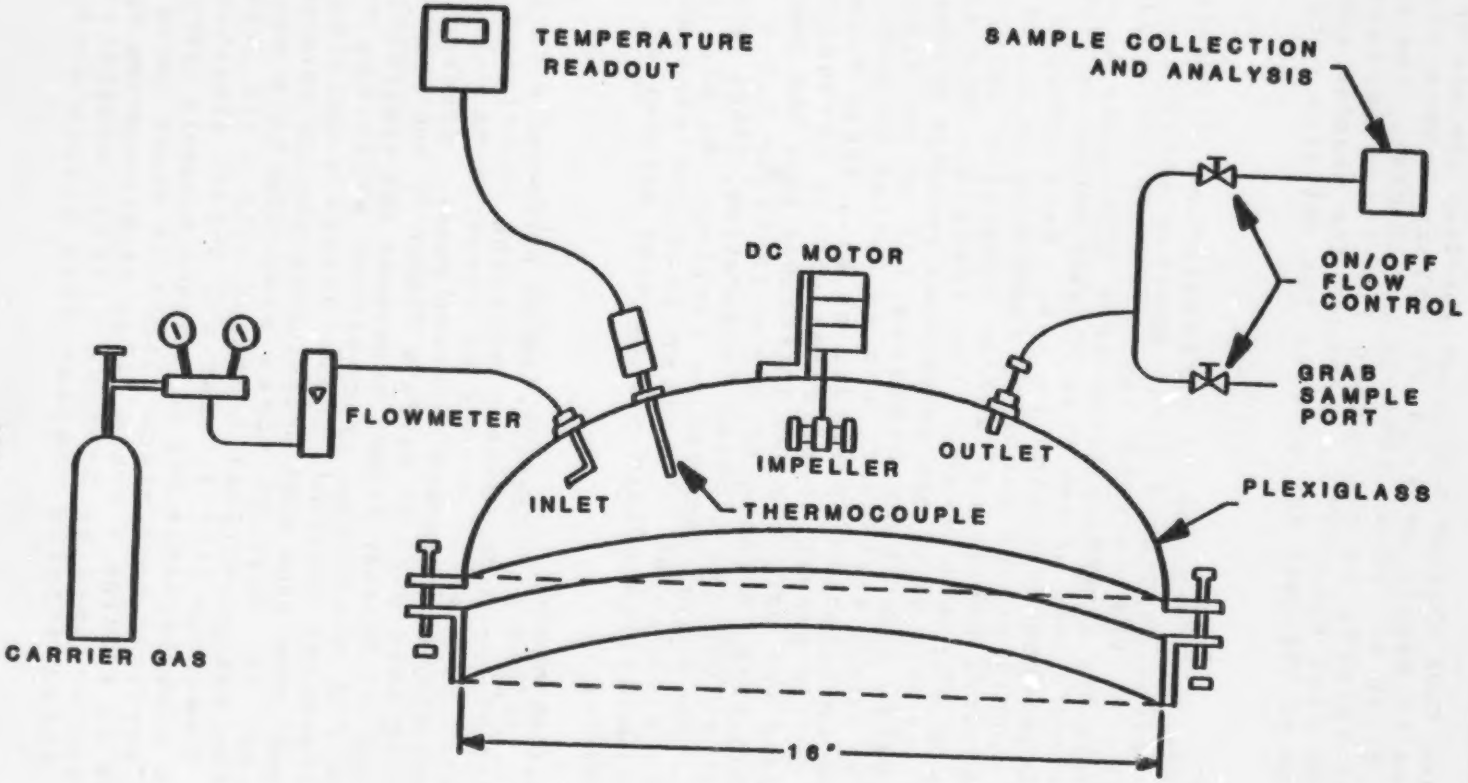

TEMPERATURE READOUT
SAMPLE COLLECTION AND ANALYSIS
DC MOTOR
ON/OFF FLOW CONTROL
GRAB SAMPLE PORT
FLOWMETER
IMPELLER
OUTLET
INLET
THERMOCOUPLE
PLEXIGLASS
CARRIER GAS
16'

Figure 4.15. Surface flux chamber and peripheral equipment (Eklund, et al., 1984).

impeller, ultra-high purity sweep air and rotameter for measuring flow into the chamber, and a sampling manifold for monitoring and collection of the specie(s) of interest. Portable FID- and photoionization detector (PID) based analyzers were used to continuously monitor total hydrocarbon concentrations in the chamber outlet gas stream. Samples were also collected for subsequent GC analysis once a steady-state emission rate was obtained. Air and soil/liquid temperatures were measured by using a thermocouple. The system pressure was monitored by using a magnahelic pressure gauge. This technique has been applied to determine the area of contamination at two jet fuel (JP-4) spill sites (Radian Corporation, 1984; Radian Corporation-T, 1984).

Limitations--The surface flux chamber technique has several limitations which should be considered prior to selection. The sweep air dilutes the gas sample which decreases the sensitivity of the method. This technique is not suited for sites with caliche or other semi-impermeable soils or when the soil sampled is saturated with water which blocks gas transport pathways. In addition, the method has an inherent effect on the emission rate being measured. These effects have been investigated (Koerner, et al., 1984; Zohdy, et al., 1974), and modified chambers have been developed [Mathis, et al. (1980)] to minimize these effects. Finally, it should be noted that gas concentrations at the surface are normally lower than at subsurface locations.

Sorbent Samplers

Sorbent samplers can be used to collect soil gases during a given time period. The sampling time is adjusted to provide a sufficient quantity of trapped gas for analysis. This technique provides an integrated sample that compensates for any short-term fluctuations in soil gas concentration.

Recommended Use--

Sorbent samplers are well-suited for almost any site. The sorbent sampler technique is best suited for cases when the soil gas hydrocarbon concentration is expected to be very low. The sampling duration can be varied to ensure that sufficient material is collected for analytical detection. This technique is useful for determining whether contamination is present, but other techniques are more appropriate for obtaining more specific information.

Technique Applications--

A wide variety of sample gas extraction and accumulation procedures have been reported. In general, they involve the addition of a sorbent sampler to sampling techniques such as ground probes, collection cans, or flux chambers.

Several researchers have used passive samplers in conjunction with ground probes to detect the presence of hydrocarbons. For example, Boys (1967) pumped sample gas from a ground probe for 30 sec to 10 min and recorded the volume. He then used his patented method of using a refrigerated GC column for analyzing the soil gases. In other work, the exhaust gas from ground probes has been trapped by using activated charcoal (Colenutt, et al., 1980), Tenax (Swallow, et al., 1983), and Draeger tubes (Walther, et al., 1983). Colenutt and Davies (1980) cite other researchers using silica gel, graphitized carbon black, and porous polymers.

Other researchers have used collection cans or some sort of enclosure to obtain gas samples. For example, Pearson, et al. (1965), pumped gas from an enclosure through a series of chilled impingers containing absorbing solution to measure the radon-222 flux from soil. During their investigation, they experienced a large variability in their results which they attributed to soil disturbance from the edge of the enclosure. Thereafter, caulk was used to seal the enclosure with the sampling surface. Kristiansson and Malmquist (1982) also measured radon by using detectors in inverted cups placed in shallow holes and refilled with soil. Ryden, et al. (1978),measured the nitrous oxide flux from soils by continuously pumping gas from an enclosure and by trapping the sample in molecular sieves. Karimi (1983) used enclosure devices to sample at hazardous waste sites. The procedure involved pumping gas out of the enclosure, trapping hydrocarbons in a column of activated charcoal, and analyzing samples by GC and GC/MS. Fluxes were measured for ten selected organic compounds and ranged from 4.3×10^{-11} to 1.2×10^{-9} lb/ft^2-sec.

McCarthy (1972) collected mercury emissions by using enclosures on the ground surface (for 2-hr periods) with an amalgamation on a silver screen placed inside the enclosure. As reported by Kanemasu, et al. (1974), some investigators have used hydroxide solutions in inverted cans to measure the carbon dioxide flux. These investigators reported that this static collection method yields fluxes 20 percent lower than a dynamic (flux chamber) method.

Rouse (1984) used a slightly different procedure to passively measure soil surface gases. Glass vials filled with an absorbing solution were buried 6 inches deep in backfilled holes and left in the field for 1 month. Rouse found that the depth at which the vial was placed (a few inches to a few yards) did not affect the results. In addition, he concluded that this procedure produced similar results to the grab

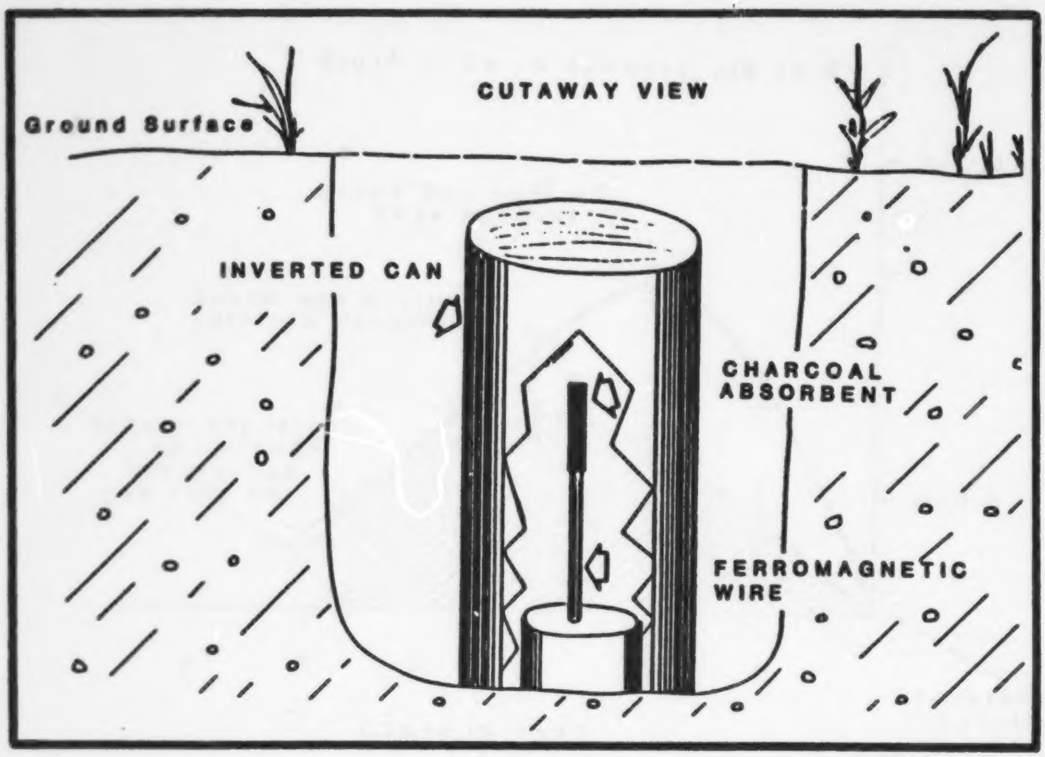

CUTAWAY VIEW
Ground Surface
INVERTED CAN
CHARCOAL ABSORBENT
FERROMAGNETIC WIRE

Figure 4.16. Curie-point wire accumulator device (Voorhees, 1984).

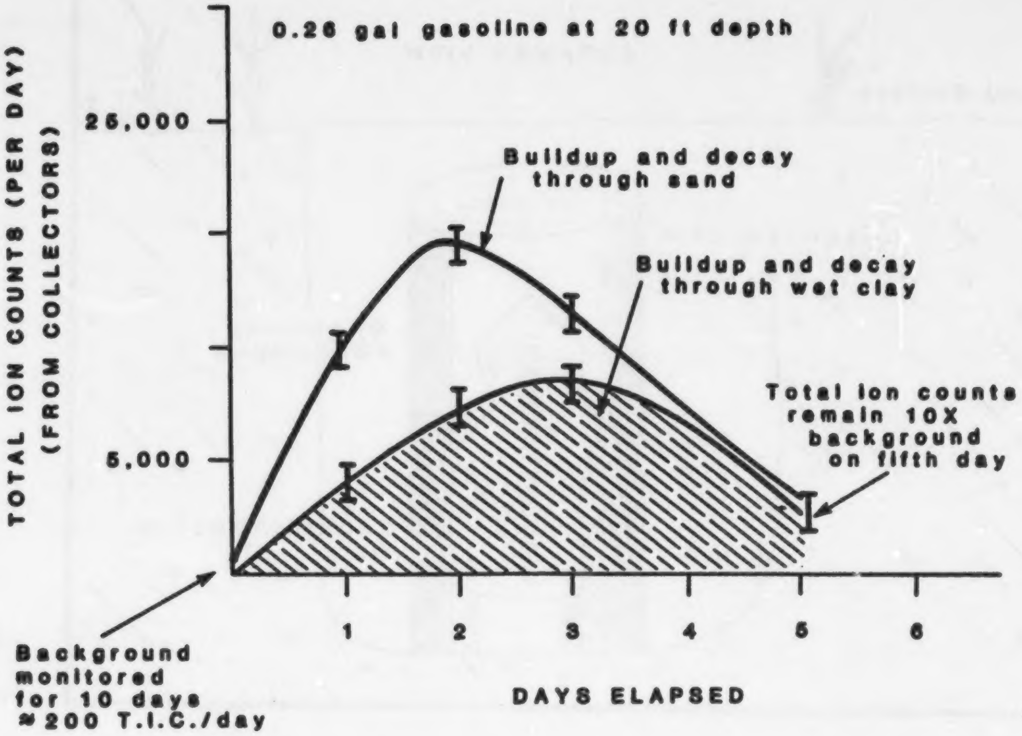


Figure 4.17. Build-up and attenuation of volatiles from gasoline through a sand column and through undisturbed wet clay soil as measured by Curie-point wire sampler (Bisque, 1984).

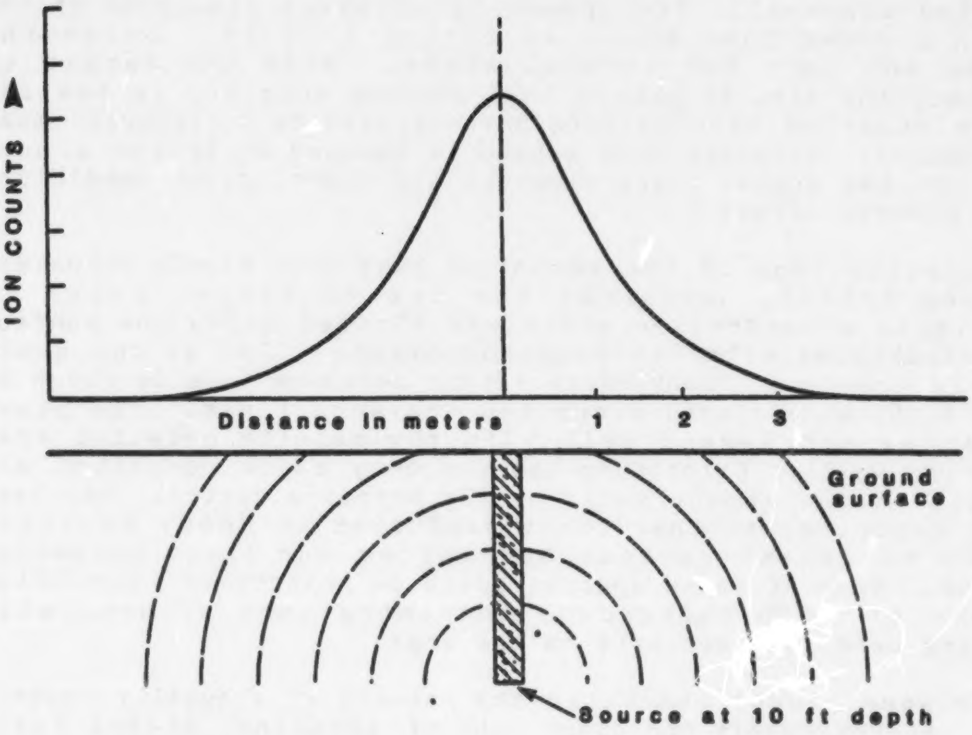

ION COUNTS
Distance in meters
1
2
3
Ground surface
Source at 10 ft depth

Figure 4.18. Hypothetical diffusion pattern (below) and measured surface flux anomaly (above) as measured by the Curie-point wire sampler (Bisque, 1984).

sampling soil core technique and to an ambient air sniffer survey.

A passive sampling technique using activated charcoal was developed by Petrex Corporation and has a patent pending. Reported advantages of this device include: (1) the samplers are simple and rugged, (2) sampling and analysis are relatively inexpensive, (3) light hydrocarbons can be detected, and (4) the technique appears to be relatively unaffected by weather and site conditions. Bisque (1984) describes the sample device as a thin ferro magnetic (Curie-point) wire coated with activated charcoal. The procedure involves placement of the wire in a glass tube which is buried 6-12 in. below the surface and left for several weeks. When the sample is retrieved, the wire is placed in a vacuum chamber, is heated, and the desorbed hydrocarbons are analyzed by Curie-point mass spectrometry. Although this method is limited by frozen ground and saturated soils, meteorological and hydrological conditions have a minimal effect.

Applications of the technique have been widely reported. Voorhees (1984), described the use of Petrex tubes to investigate ground-water which was 44-feet below the surface and contaminated with tetrachloroethylene (TCE) at the Rocky Mountain Arsenal. Twenty-five Petrex samplers (one is shown in Figure 4.16) were placed along two traverse lines. The plume boundaries and agreed well with the results obtained from monitoring wells. Chloroform was the only major component not detected in the ground-water by the trapping device. Voorhees (1984) described another study conducted at Rocky Mountain Arsenal to detect various hydrazines and their oxidation products. None of these species could be positively identified because of high background concentrations of naturally occurring petroleum deposits in the area.

Bisque (1984) presented the results of a quality control study. Approximately one quart each of gasoline, diesel fuel, and crude oil were introduced at 10-foot depth in soil media that varied from tight clay containing 10 percent free water to dry colluvial material. In all cases, trace emissions were detectable at the surface within hours. Figure 4.17 shows concentration versus time data for each soil type. Contamination could still be detected after 60 days. The observed diffusion pattern from the point source contamination is shown in Figure 4.18.

Limitations--The Petrex tube sampling technique and other passive techniques require a long sampling time and disturb the sampling site. In addition, high background concentrations may interfere with obtaining accurate measurements. The efficiency of this collection method cannot be determined since, unlike the surface flux chamber technique, the sample enters the tube by passive diffusion, and the volume of gas sampled is not measured.

Sample collection by pumping soil gas from collection cans or ground probes also has limitations. The pumping may disturb the equilibrium between the soil gas and the gas sorbed on soil particles. It may cause dilution and/or contamination of the sample by ambient air.

Kerfoot and Mayer (1986) give the following limitations for passive charcoal soil-gas samplers with analysis by thermal description: it is not quantitative, there may be thermal decomposition of tightly sorbed and less volatile compounds, and chemical decomposition of the samples is promoted.

SAMPLING DESIGN AND SAMPLING QUALITY ASSURANCE TECHNIQUES

This section discusses the approach necessary to make optimal use of the available resources and to ensure adequate data quality when making soil-gas measurements.

Sampling Strategy

The sampling strategy should be devised to obtain all necessary and required information with a minimal expenditure of time and resources. Prior to developing a sampling strategy, any available information pertaining to the following items should be collected and evaluated: type of contaminant present; amount of contaminant present; length of time contaminant has been present; direction and rate of flow of ground-water; depth to ground-water; geological soil properties of the site; number, type, and location of existent subsurface structures (e.g., wells and sewers); existent sampling and analytical results; and any anecdotal evidence of contamination.

The above information, along with the objectives of the test program, should be used to tailor a sampling strategy to the specific circumstances encountered. An example contamination problem is discussed below and serves to illustrate the process of developing a sampling strategy. Examples of specific sampling strategies may be found in the references to the individual sampling methods discussed in Section III.A.

At a hypothetical site, an underground storage tank containing industrial/organic wastes is suspected of leaking based upon inventory control records and tank-tightness tests. Little information is available regarding the site, and no existing observation wells are present. Furthermore, nearby wells (approximately 1 mile distant) in every direction provide community drinking water, and the press is aware of the situation. The objective is to determine the extent of any contaminant plume.

The first step after background information collection and evaluation is to establish a grid system over the site with the suspected source at the center. The number of points that should be sampled is very site and project specific. The number will depend on the resources available, the project objectives, and the level of risk that is acceptable. In general, it is much more resource-intensive to prove that an area is not contaminated than to roughly delineate the extent of a contaminant plume. In our example, a grid of 10 rows of 10 sampling points each with points and rows separated by 50 feet might be used. Once all the design considerations discussed below had been met, measurements made at approximately a dozen selected sampling points circumscribing the point source would indicate the direction of any contaminant plume. A more refined secondary phase of sampling could then be planned. A transect of equi-spaced sampling points in the direction of the plume would indicate the location of the plume front. Once this has been determined, several lines of equi-spaced sampling points perpendicular to the transect line will indicate the lateral extent of the plume.

The next consideration is to select a sampling method. The selection will depend upon the contaminant species, the site characteristics, the expertise available, and any time and budget constraints. In the example case, a sampling and analytical system such as ground probes and on-site analysis of the gas samples might be selected to provide rapid feedback to site investigators.

A third consideration is what species to monitor. This is, of course, dependent on the sampling method selected. The choice (tracer gas) should be a compound that is detectable at low concentrations, has low molecular weight so that it will be present near the plume front, but not so light that it is rapidly lost to the atmosphere. The tracer gas should be relatively inert and insoluble in water so that attenuation is not a problem. Finally, the tracer compound must be readily attributable to the contaminant plume and not to background sources or analytical interferences. In our example, a compound would be selected that was typically present in the storage tanks. Good candidates might be a chlorinated solvent such as TCE, benzene, or total hydrocarbons.

A fourth consideration is the selection of a sampling horizon or depth. Soil-gas measurements are typically made at depths from 0 to 10 feet unless existing wells are present. Sampling at depths below 10 feet negates the advantages in terms of time and effort of using soil-gas measurements relative to other options. Certain sampling methods such as surface flux chambers or Curie-point wire samplers can be used at or near the surface. Other methods, such as ground probes, can be used at variable depths. When using ground probes, it is recommended that several vertical profiles be performed at sampling points known to be contaminated. This information can then be used to select a sampling depth that yields conclusive results for subsequent sampling points. In our example, ground probes would be driven to 6 to 10 feet until contamination is first encountered. Once a contaminated point is found, additional ground probes could be driven nearby. Samples collected at one-foot depth intervals would then show what a suitable sampling depth would be. It is useful, during subsequent sampling, to periodically perform vertical profiles rather than always to sample at a fixed depth. The vertical profiles will indicate whether the typical sampling depth should be modified; deeper to improve sensitivity, or shallower to improve productivity.

A final consideration is the length of time spent sampling at any given point. This is dependent on the sampling method selected and on the sensitivity desired. Methods that require a probe/sampler to be placed in the ground may result in a disturbance of the equilibrium among free product, adsorbed product, and gas in the soil-pore spaces. The time required to allow this equilibrium to be reestablished prior to initiating sampling can be as much as one day. Also, for methods such as accumulator devices, the sampling duration can be extended to lower the detection limit of the method. The final choice of sampling duration must be based upon experience, preliminary results, and site and project specific factors. In our example, since absolute concentrations are not required, the ground probes could be driven to the desired depth, allowed to equilibrate for as little as one hour, and then the samples could be collected.

Quality Assurance

This section addresses sampling quality control. Analytical quality control is discussed in the next chapter. Quality control must be an integral part of any sampling plan and is necessary so that the results obtained for the project are meaningful, i.e., the data are of a known quality. The exact quality control checks required for any project will be dependent on the sampling and analytical methods selected. The following list of quality control considerations is applicable to most soil-gas measurement programs:

- detailed sampling procedures and schedules clearly written and consistently followed;
- samples labeled with all pertinent information;
- data collected on appropriate data sheets and reviewed daily;
- sample logs, chain-of-custody forms, and other paperwork kept up-to-date and reviewed daily.
- sampling blanks collected at least daily;
- repeat measurements at a control point;
- background measurements made at least daily;
- a minimum of 10 percent of samples collected in duplicate; and
- a minimum of 10 percent of samples analyzed in duplicate.

The value of keeping good records and of using a consistent technique is obvious. Sampling blanks are useful for detecting contamination within the sampling system that would not be detectable from analytical blanks. Background measurements allow comparison to measurements in the contamination zone to ensure observed contamination is not due to problems with the sampling method or implementation.

Duplicate and repeat sampling permit statistical analyses to determine the variability associated with the sampling procedure. For sites where the temporal variability exceeds the spatial variability, repeat sampling may be replaced with side-by-side duplicate sampling. Side-by-side samples should be expected to show greater variability than repeat sampling since no two discrete sampling locations are perfectly identical. With the sampling methods that require the sampling location to be disturbed, e.g., ground probes, the side-by-side sampling locations must be sufficiently separated so that the placement and sampling at one probe does not effect the soil gas concentration at the adjacent probe. This distance will vary depending on the soil characteristics, but should be assumed to be at least 3 feet.

When employing sampling methods that permit the reuse of sampling components for multiple sampling points, care must be taken to avoid cross-contamination of samples. This can best be prevented by cleaning sampling components before each sampling point and by performing sampling blank and background measurements after any measurements showing high levels of contamination. Should the blank/background data show a significant contamination problem, the sampling components need to be thoroughly cleaned and retested, or replaced.

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CHAPTER 5

ANALYTICAL METHODOLOGIES

SELECTING THE PROPER METHODOLOGY

The method chosen to analyze soil gas is dependant on the pollutant being monitored, the concentration of the pollutant, the matrix accompanying the pollutant, and the information expected to be obtained from the analytical results. Expected concentrations for organic species in soil gas can vary from the ppt (trillion) volume level (well below most analytical detection limits) in background measurements to high percent by volume levels in a measurement made directly over a highly volatile liquid lens such as gasoline. The concentration level actually measured will depend on the sampling method and on the amount of dilution or concentration which occurs during the sample collection. Flux chamber methods dilute the soil gas while accumulator device methods concentrate the soil gas components. The analytical sensitivity of the method chosen for soil gas analysis must be consistant with the sampling method, the soil type, pollutant quantity and volatility, ground-water plume depth, and the data requirements. Measuring emission rates at the surface with acceptably low variance or mapping the fringe of a plume at the surface where the plume is of low volatility, is at a great depth, or where the soil has a high adsorptivity or low permeability, would require a very sensitive analytical technique. The same technique would need to be greatly modified to analyze a sample over a gasoline plume in sandy soil.

In some cases, the pollutant species which requires monitoring is not the major component in the soil gas, and the determination of that species is complicated by the sample matrix. A very sensitive technique may not be appropriate if it responds to the components in the matrix as well as the species of interest. In such cases, selectivity is required and can be obtained by isolating the desired species during collection, separating the desired species from the sample matrices during the analysis (i.e., chromatography), or detecting only the compound of interest (selective detection). Specific exam-ples of such cases are concentrating hydrocarbons on a porous polymer absorbent while excluding the highly volatile hydrocarbons, permanent gases, and water; using high resolution capillary columns to separate benzene from other hydrocarbons in gasoline; and detecting trace levels of toxic halogenated compounds in soil gas by using an electron capture detector or a Hall Electrolytic Conductivity Detector (HECD).

In addition to sensitivity and selectivity, several other considerations are required to determine the degree of analytical sophistication that is needed for a specific measurement. The questions that need to be asked are listed below.

(1) Is detailed speciation required or will a total organic value provide the data required?

Sometimes a total organic value is all that is needed to monitor the movement of a ground-water plume or to determine the emission rates from surface or downhole emission experiments. Detailed speciation is required if the migration and flux rates of individual components are desired. Often a few detailed speciation analyses can be used as a profile, and individual results can be extrapolated from total organic values.

(2) Is the analytical technique to be used to determine the relative concentration or will absolute concentration values be required?

Real-time portable analyzers (e.g., FIDs and PIDs) are very cost effective and easy to use for obtaining relative levels of organic compounds of similar compositions. This can be extremely useful in screening the sampling points before deciding on more resource intensive remote analysis or before plotting the relative concentration across a homogeneous plume. If the sample components in the plume vary with distance or depth, the portable analyzer can fail to give correct relative values as will be shown later.

(3) If the samples collected are to be analyzed in the lab, will the sample require that the lab be on site or can it be in a centralized laboratory remote from the sampling site?

This question is dependent on two factors: the stability of the components of interest and the analytical sophistication required to do the analysis. If the sample's shelf life is less than 24 hours, then analysis must be performed in the field. If the analysis is so complicated that logistics or cost prohibit its use in the field, then the sample will have to be sent to the lab. When a sample cannot be stored for transport to the lab or the analysis is too complicated to take to the field, another method for analysis or sampling must be used.

Portable VOC Analyzers

The use of portable VOC analyzers for fugitive emission screening, source identification, and industrial hygiene monitoring has proven to be very valuable, and they have also been used to analyze VOCs in soil gas. Of the commercially available portable analyzers, several types are useful for soil- gas measurements. These are the nondispersive infrared detectors, flame ionization detector (FID) analyzers, and the photoionization detector (PID) analyzers. The manufacturer's descriptions of selected portable analyzers are given in Table 5.1. These portable analyzers generally provide real-time measurements without performing separations; however, some have chromatographic capabilities as an option. The advantages of portable analyzers include:

- The analyzers are easy to transport in the field.
- The operation of the analyzer requires minimum operator skill.
- The elimination of the sample collection steps minimizes the uncertainties and expense of sample collection, storage, and transport.
- Data are provided immediately which enable the investigators to make timely discussions in the field.

The disadvantages of the portable analyzer include:

- The limited sensitivity because of the lack of a concentration step.
- The limited selectivity and interference problems because of the lack of a separation step.
- The limited accuracy because of the inability to calibrate adequately for the mixtures found in soil vapors.

The various analyzers on the market (Anastas, et al., 1980) have their unique advantages, disadvantages, and areas for use as monitors of soil gas for VOCs. The following section will discuss the types of analyzers best suited for soil gas analysis.

FID analyzers--

The FID is the most widely used detector for the analysis of VOCs by gas chromatography. It is also one of the most widely used for portable analyzers. The Century Organic Vapor

TABLE 5.1. DESCRIPTION OF SELECTED PORTABLE ANALYZERS

	Century System	HNU	Analytical Instrument Development, Inc.	Photovac, Inc.	Bacharach	Miran
Model	OVA-108	PI 101	580	TIP	TLV Sniffer	1B
Technique	Flame Ionization	Photoionization	Photoionization	Photoionization	Catalytic Combustion	Infrared
Precision	±10%	±1% of FS	±1% of FS	±1%	-	-
Sensitivity	1 ppmv (methane)	0.2 ppmv (benzene)	0.1 ppm (benzene)	0.05 ppm (benzene)	2.0 ppm (hexane)	-
Response Time	2 sec	<5 sec	2 sec	-	-	-
Range	1-10,000 ppmv, 1-1000,000 ppmv logarithmic	0.1-2000 ppmv	0-200 ppm 0-2000 ppm	0-2000 ppm	0-100 0-1000 0-10,000 ppm	ppb-%
Sample Flow	1 L/min	Low (<0.5 L/min)	0.5 L/min	0.275 L/min	2 L/min	-
Power Supply	DC	AC/DC	AC/DC	DC	DC	DC
Service Life (continuous use/charge)	8 hrs	10 hrs	8 hrs	4 hrs	8 hrs	4 hrs
Weight	14 lbs	9 lbs	8.2 lbs	3 lbs	5 lbs	28 lbs
Approximate Cost	$5,200	$3,200	$3,900	$3,300	$1,500	$12,500
Contact Information	(617) 543-8750	(617) 964-6690	(215) 268-3181	(516) 351-5809	(412) 963-2235	(617) 543-8750

Analyzer (OVA) is an example of an FID instrument. The FID responds to organic compounds with a sensitivity of <1 ppmv for methane but does not respond to inorganic components in air. The Century OVA can be operated continuously with a sample probe collecting a sample at approximately 1 to 2 L/min or as a GC with an isothermal (ambient or ice bath) column and with gas sampling valves. The total range can be scaled to 3 ranges or as a single scale from 1 to 10,000 ppmv and higher by using a dilution probe. The OVA is powered by a battery pack and contains a hydrogen tank which supplies the fuel for the FID. The FID oxidant is ambient air.

An advantage of the OVA is its response to a wide range of organic compounds with sub-ppmv sensitivity. It is also easy to use, has a wide range, and has optional chromatographic capabilities. The greatest disadvantage of the OVA is its variable response to different organic compounds. Several studies have been made to determine response factors for organic species (Brown, et al., 1980; Dubose and Harris, 1981; Dubose , et al., 1981; Willey, et al., 1976). The response factors were found to vary from 0.2 to more than 100. Table 5.2 shows how the varying response factors affect the concentration reported by the OVA. The large range in values reported in Table 5.2 also indicates the OVA response is highly variable. The equal carbon response typical of the FID is not found for the OVA when used in the non-chromatographic mode. However, hydrocarbons display less variation than organic compounds containing heteroatoms such as oxygen or nitrogen as shown in Table 5.2. Using an OVA for gasoline detection would result in smaller errors due to calibration than other portable analyzers. The OVA has been used extensively for gasoline detection.

This problem of calibrating the OVA can be minimized by using the GC option and by calibrating for each individual compound. However, environmental samples contain such a large number of components that adequate chromatographic separation cannot be obtained with the ambient temperature OVA column. Another disadvantage of the OVA is the high sample flow required (1 to 2 L/min). For soil-gas measurements such as soil-core or ground-probe measurements, removing soil gas at this rate would be difficult without disturbing the soil/gas equilibrium or drawing in air from above the soil. The sensitivity of flux chamber measurements will be limited by the OVA since the diluting sweep gas flow rate needs to be equal to or greater than the OVA sample flow rate.

Despite the problem mentioned above, the OVA has been used successfully as a screening tool for ground-probe measurements, to correlate other measurement techniques (Glacum, et al., 1983), to determine when steady-state

TABLE 5.2. INSTRUMENT RESPONSE TO SELECTED ORGANIC COMPOUNDS

Family/Compound	Actual Concentration (ppmv) Required to Cause a 10,000 ppmv Instrument Response* OVA
Alkanes/Ethane	6,500 (4,400 to 15,800)
n-Butane	5,000 (4,600 to 5,500)
n-Hexane	4,100 (3,800 to 4,500)
Cyclo-alkanes/ Cyclohexane	4,700 (3,900 to 5,800)
Alkenes/Ethylene	7,100 (6,300 to 8,200)
1-Butene	5,600 (5,100 to 6,200)
1-Hexene	4,900 (3,900 to 6,600)
Aromatics/Benzene	2,900 (2,800 to 3,100)
Toluene	3,900 (3,600 to 4,300)
o-Xylene	4,300 (2,800 to 8,500)
Alcohols/Methanol	43,900 (36,100 to 56,000
1-Propanol	9,300 (7,700 to 11,600)
1-Butanol	14,400 (8,900 to 23,400)
Acids/Formic Acid	142,000 (106,000 to 198,000)
Acetic Acid	16,400 (11,100 to 26,500)
Butyric Acid	8,000 (3,800 to 31,400)
Halogenated Compounds/ Chloroethane	53,800 (18,700 to 264,000)
1,1-Dichloroethane	7,800 (6,200 to 10,200)
1,1,2,2-Tetrachloroethane	78,900 (50,100 to 138,000)

*Both instruments were calibrated to methane at 8,000 ppmv (Dubose, et al., 1981).

conditions have been reached in flux chamber experiments (Radian Corporation, 1984), and to adjust the sweep-air flow rate to achieve the desired concentration range in flux chamber experiments. When using the OVA for these purposes, one should remember that changes in concentration readings could be due to a change in the organic composition instead of a change in the actual concentration. Likewise, a stable concentration reading may be due to a change in the total organic concentration complemented with a change in composition. However, in cases where the composition of the ground-water plume is homogeneous, the OVA should provide a convenient screening tool of the relative total organic concentration.

PID analyzers--
The PID has become popular as a detector for portable analyzers because of its high sensitivity to certain compounds, its ease of operation, and because no fuel gas or flame is required.

The PID ionizes compounds whose ionization potentials are close to or lower than the energy of the lamp used. Different energy lamps are available for analyzing different compounds allowing for some selectivity. With the 10.2 eV lamp, alkanes have little or no response while alkenes, aromatics, organosulfur compounds, and carbonyl compounds have high responses. Alcohols, halogenated alkanes, and most inorganic gases have no response. With a 11.7 eV lamp, all of the selectivity for organic compounds except methane is lost. The reported sensitivities for benzene are 0.1 ppmv in air and have a range up to 2000 ppmv for benzene. Another feature of the PID is that it is essentially a non-destructive detector which allows samples to be collected after passing through the detector.

The three major portable analyzers available are the Photovac 10A10 portable GC, the HNU photoionizer, and the AID Model 580 PID system. The Photovac is designed as a GC but can be operated in a continuous mode with the addition of a pump. Samples are injected into the column and are separated by using a dry air carrier gas. Packed columns up to six meters in length and capillary columns can be used in the portable GC. Sensitivities down to 0.1 ppbv for hydrogen sulfide are quoted by the manufacturer. Photovac also now markets a portable PID instrument called "TIP" for gas analysis which is designed to be used as a continuous analyzer.

The HNU photoionizer is a continuous analyzer with the lamp contained in the sample probe. The small probe volume allows the detector to respond in as little as 3 seconds and requires only a small sample size. The sample flow rate is approximately 0.5 L/min. Three lamps (9.5 eV, 10.2 eV, 11.7

eV) are available. The AID 580 is similar to the HNU except the lamp is enclosed in the unit and is not in the probe. The sample flow rate is approximately 0.5 L/min, and the exit is plumbed for easy collection of samples for laboratory analysis.

The advantages of the PID analyzers are the greater sensitivity for many compounds compared to the FID, the selectivity for certain classes of compounds, the nondestructive nature of the PID, and the absence of fuel gas. The disadvantages are the highly variable response factors for each compound, matrix effects such as quenching of the response because of oxygen (Freeman, 1980), and the low response or lack of a response for some compounds such as the fluorocarbons. The Photovac used with a column could minimize some of these problems.

The usefulness of the PID analyzers is in screening soil vapors containing non-methene hydrocarbons in the presence of high levels of methane or when ambient levels of methane interfere with monitoring low levels of nonmethane pollutants. They can be used to screen for compounds by class such as aromatics and organosulfur or for individual components such as vinyl chloride. As with the FID analyzers, the values obtained for the PID should not be considered absolute. When the response is used as a relative value, the organic composition and matrix must be homogeneous over the area or time being compared.

Other analyzers--

Two other types of portable analyzers have been used to detect trace levels of VOCs in air. The long-path-length IR analyzers have sensitivities in the low ppmv. The MIRAN-IA gas analyzer has a variable path length cell (range 0.75 m to 20 m) so that a range from less than 1 ppmv to 10,000 ppmv can be analyzed. The wavelength is also variable and allows for moni-toring almost any organic component. A microprocessor model can be used to monitor up to 11 components. The analyzer is concentration-dependent and has a sample flow rate of 30 l/min.

The advantage of the MIRAN-IA portable analyzer is the ability to monitor many of the reactive organic compounds such as phosgene, ethylene oxide, and formaldehydes which are difficult to sample and to analyze with other techniques. The disadvantage of the MIRAN-IA is the large cell volume which is required for ppmv measurements. A large volume of soil gas is needed to obtain that kind of sensitivity. Such a volume is seldom available except with diluted flux chamber measurements. Total organic values are relative at best, while individual compounds can be selectively monitored and quantitated at the chosen wavelength. The MIRAN-IA portable model weighs 32 pounds which is substantially more than the PID and FID analyzers. In addition, the stability and the ruggedness of the optical analyzers would be expected to be less than the FID or PID analyzers.

Another commonly used portable analyzer is the Bacharach TLV Sniffer. It is a hot-wire detector which measures vapors which can be catalytically combusted. It has a range of 2 ppmv to 10,000 ppmv and a nominal sample flow rate of 2 L/min. Like the FID, the TLV Sniffer responds similarly to all organic compounds and has variable response factors (Brown, et al., 1980; Dubose, et al., 1981). As a result, it has the same advantages, disadvantages, and uses as the FID analyzer listed above.

Conclusions--

The portable analyzers designed for ambient-air analysis have limited uses as analyzers of soil gases. Their advantages are the elimination of sample collection and transportion, and theimmediate availability of results. The major disadvantages are variable response to different classes of compounds and large sample volume requirements. Having a detection limit of 1 ppmv can limit use in some cases. The uses for portable analyzers include screening wells and ground probes to determine if more accurate and expensive sampling efforts are needed and to optimize flux chamber conditions before collecting a sample for detailed analysis.

Remote analysis--

In almost all cases, to accurately determine the amount or composition of organic compounds in soil gas, a sample has to be collected and taken to a laboratory where conditions are stable enough to support the level of sophistication required to analyze the sample. The laboratory could be a mobile field lab on the site or a modern analytical lab on the other side of the country. With either situation, a representative sample must be collected, and its integrity must be maintained until it can be analyzed. The sampling method must be compatable with the analytical method. If the analysis is not very sensitive, a large sample must be collected. If the sample must be sent across the country, the container must be inert and rugged. The following sections will discuss first the sample collection and storage methods and then the analytical methods which are used or could be used for soil-gas measurement.

Sample collection--

Sample collection methods of VOCs in gases are divided into two classes:

- Adsorbent methods where the gas is passed through a solid adsorbent which removes the VOCs from the inorganic gas matrix.
- Whole air methods where the entire sample is placed in a container and is transported to the lab;

Adsorbent methods--The adsorbent method is attractive because it concentrates the components of interest and removes many of the components known to add to the instability of the sample and which interfere with the sample analysis. The adsorbent containers are generally small and can be easily transported to and from the field. The limitations of the adsorbent methods are irreversible adsorption, incomplete adsorption (breakthrough), and artifact formation. Irreversible adsorption occurs when adsorbed components cannot be completely desorbed. Ideally for the analysis of VOCs, adsorbents should be thermally desorbed since solvent desorption increases artifacts, dilutes the sample components, and interferes with the analysis. Incomplete adsorption is characterized as a breakthrough and results in the loss of the more volatile sample components. Artifact formation can occur during thermal desorption or from reaction with the adsorbent material and the sample. All three of these possible problems must be fully investigated during the sampling method validation, and a strict quality control plan must be followed to insure the method is performing within acceptable limits

The adsorbent materials most often used for sampling VOCs are activated charcoal and porous polymers such as Tenax. Other adsorbents which have been used are molecular sieves, silica gel, and activated alumina. Charcoal has been used extensively in industrial hygiene application for monitoring VOCs, and NIOSH has published a standard method for charcoal (White, et al., 1970; NIOSH, 1974). Charcoal has a high adsorbent efficiency for all organic compounds but requires solvent desorption. Desorption efficiencies can vary with the lot of the manufacturer (Saalwaechter, et al., 1977). Carbon disulfide is used as the solvent and interferes with the determination of components more volatile than n-butane. Since the solvent cannot be concentrated without volatile loss, the sensitivity of the method is limited. The use of charcoal as an adsorbent for soil-gas collection has been reported by Colenutt and Davies (1980) and Karimi (1983). A patented method using a Curie-point wire coated with activated charcoal is used by Petrex Corporation (Bisque, 1983). Instead of passing the sample through an adsorbent bed, Petrex allows the sample to diffuse into the coated wire over 3 to 15 days. The wire is then analyzed by Curie-point mass spectrometry. The technique is very sensitive and does not affect the gas/soil equilibrium. Absolute quantitation determined by using this technique is difficult, and long sampling times are required to obtain high sensitivities.

The porous polymer adsorbent Tenax-GC has been used extensively in ambient air measurements. Several good reports have characterized the breakthrough volumes for a large number of compounds, the affect of moisture and sample flow, of desorption efficiency, and of artifact formation (Brown and Purnell, 1979; Krost, 1982). Tenax has been found effective for most organic compounds except for hydrocarbons and halocarbons that are more volatile than n-hexane, low molecular weight alcohols, amines, and aldehydes. Compounds can effectively be thermally desorbed to obtain sub ppbv detection limits. Varying amounts of artifacts have been reported for Tenax; some of them are believed to be due to oxidation of Tenax and to improper cleaning of the adsorbent. Because of the artifact peaks and the inability to trap the less volatile compounds, Tenax cannot be used to obtain total VOC values, but it would be an ideal method to monitor individual components when it is shown that they are not affected by these problems. Tenax-GC has been used to analyze soil gas from ground probes. Swallow and Gschwend (1983) monitored benzene, toluene, and trichloroethylene in ambient air and at two depths in the soil above the ground water. They reported values as low as 0.2 ng/L with a precision of ±15 percent.

Whole air methods-- Whole air methods of analysis of VOCs in soil gas have been used extensively. The method could be divided into two subcategories. One involves removing the soil gas from the soil and transporting it to the lab, and the other involves transporting the soil with the gas. For collection of soil gas, three different containers can be used:

- plastic bags made of Tedlar or Teflon,
- passivated stainless-steel canisters and syringes, and
- glass syringes.

When evaluating which container to use, several factors should be considered:

- Sample hold time and stability over the hold time
- Sample handling and shipping and the durability of the container.
- Sample container cleaning procedures and memory effects.

The use of plastic bags for air samples is inexpensive and convenient. However, several studies have been made using Tedlar and Teflon bags (Seila, et al., 1976; Lonneman, et al., 1981) and have found that contamination was significant if the bags were exposed to light. Other problems found with plastic bags are permeation of compounds into and out of the bags during storage and sample leakage encountered during handling and transportation. Plastic bags are not recommended for soil-gas analysis unless the storage times are less than 4-8 hours and the concentrations are high.

Stainless-steel canisters with a passivated interior surface have been used for a wide variety of VOC measurements including soil-gas monitoring. The canisters have been described by Harsch (1980), and hydrocarbon, halocarbons, and carbonyl compounds have been found to be stable for as long as three weeks (Oliver, et al., 1985; Westberg, et al., 1982). The canister can be pressurized to hold more than 20 L of sample and can be shipped easily without any sample loss. The canisters can easily be cleaned since they withstand temperatures up to 150°C and can be evacuated to very low pressures. Because no light can enter the canisters, the possibility of photochemical reactions is minimized. The passivation process used to produce canisters has been applied to the production of stainless-steel syringes (Scientific Instrument Specialist, Inc., Moscow, Idaho). These syringes would have the same advantages as the canisters plus the added value of easy sample collection. A soil-gas sample could be drawn slowly when the syringe is used with the disruption of the soil-gas equilibrium being minimized. Slowly drawing a small sample when a canister is used requires vacuum flow regulation. Sample dilution is required to obtain samples smaller than canister volume (generally greater than 0.5 L).

There are two methods for collecting a sample in canisters. One involves using a pump to fill the canister. This technique requires a clean, inert pump and enough sample to purge the canister before filling it. The other method is to first evacuate the canister and then to bring the canister to atmospheric pressure with sample. The first technique would not be compatible with most soil gas techniques except flux chamber methods. The second method has been found to work for both ground probe and flux chamber methods (Radian Corporation-S, 1984; Crow, et al., 1985; Radian Corporation-T, 1984). By using a vacuum flow regulator, the rate of sampling can be controlled to minimize both soil/gas equilibrium disturbances and migration of atmospheric gas into the sampler. Detection limits of 1 ppbv have been obtained by using the canister method.

Glass containers such as syringes (Radian Corporation, 1984; Thorburn, et al., 1979; Marrin, et al., 1984; Radian Corporation-S, 1984; Crow, et al., 1985; Radian Corporation-T, 1984; Wood, et al., 1980; Dowdell, et al., 1972) and evacuated flasks (Thorburn, et al., 1979) have been used to collect soil-gas samples. Glass has been found to be inert and noncontaminating for most organic compounds. Most glass syringes and flasks require a Teflon valve or seal to be gas-tight. However, the Teflon can be a source of contamination. Ground-glass joints have been used; however, they are not completely gas-tight, and samples cannot be stored for any length of time. Because of the fragile nature of glass, it cannot be shipped very easily and is used mostly for on-site analyses. Since glass can transmit light, it has been suggested that samples could be affected by photochemical reactions and should be kept out of direct sunlight.

Another method for sampling soil gases is to pump the soil gas directly into a sample loop for injection into the GC (Weeks, et al., 1982). This requires a large volume of soil gas from a vacuum pump. This would disrupt the soil/gas equilibrium and can pull in atmospheric gas around the ground probe.

The collection of soil cores is described in chapter 4 (Head-space Measurement) and is an alternative to collection of soil gas alone. The soil cores are sealed and are sent to a laboratory where soil gas can be removed and analyzed. The advantages of this technique are that the soil itself can also be analyzed by other physical or chemical methods, the technique requires relatively little expertise or equipment, the samples appear to have a long shelf life, and a more accurate soil gas measurement can be obtained under laboratory conditions than in the field. The disadvantage of this method is loss of volatiles during the coring of the sample and transport. In some cases, obtaining a representative sample may be difficult. The sample can also be affected by biological activity in soil.

Sample Analysis--

Analysis of soil-gas samples is performed in either an on-site mobile laboratory or a remote laboratory. The instrumentation of the mobile laboratory is limited to equipment which is easily set up, rugged, and requires a minimum amount of power and support equipment. Methods which require subambient temperature programming, cryogenic concentration, and detectors with vacuum systems such as mass spectrometers are generally excluded from mobile laboratories. Theoretically, any instrument discussed here can be made mobile, but experience has shown that it is only cost effective to use an instrument specifically designed for the mobile laboratory.

Mobile laboratory instruments--The simplest mobile laboratory instruments are the portable analyzers which have chromatographic options. This includes the Photovac with a PID and the Century OVA with a FID. These have simple injection systems, either a gas sampling valve (OVA) or a syringe injection port (Photovac). The Photovac has an internal column space which can hold a 1/8" column up to 6 meters long or a 25 meter capillary column. There is no temperature control for the column. The OVA has an external column which could be of any size and is at ambient temperature. These instruments are easy to transport and use and, in the case of the Photovac, can be very sensitive with ppbv detection limits. The added advantage of the chromatographic capabilities is that individual compounds may be monitored and quantitated with accurate response factors. Because of the complex nature of most environmental samples including soil gas, the uncontrolled temperature of the column in these portable analyzers does not allow the high resolution separation needed to identify and to quantitate for most components accurately. Reproducible retention times are difficult to achieve in the field because of temperature fluctuations, and separation of components with a wide range of volatilities is difficult without temperature programming. These analyzers can be useful if the sample contains large amounts of easy to separate contaminants such as those found in a chemical spill or if only a volatility range is needed such as total C2-C4 compounds. Gasoline samples are often characterized by comparing the function of the total organic compounds in volatility range.

A step above the portable GCs are the field GCs. These are small, sturdy GCs that contain temperature controlled ovens and a variety of injectors and detectors. Some of the modules which have been used for soil gas are the Varian Mobel 6000 (Marrin, et al., 1984), Shimadzu Model GC-Mini 2 (Radian Corporation, 1984; Radian Corporation-S, 1984; Radian Corporation-T, 1984), Carle AGC (Wood, et al., 1980), and the HNU GC 301 (Radian Corporation-S, 1984). Table 5.3 contains the descriptions given by the manufacturers of selected portable GCs. This list is not exhaustive and does not mean to exclude other GCs which could just as easily be used in the field. The components of the GCs such as injection ports and detectors can usually be selected. In some cases, temperature programming is available. Because these GCs are smaller than standard models, the number of columns and their lengths can be limited. The best results are obtained with an instrument having a heated gas sampling valve for injection of the gas samples. The detectors most commonly found are the FID, PID, and the ECD. The HNU GC 301 is unique in that it has both an

TABLE 5.3. DESCRIPTION OF SELECTED PORTABLE GAS CHROMATOGRAPHS

	Shimadzu	HNU	Photovac	Sentex	AID
Model	GC-Mini 2	301	10510	Scentor	910
Detectors	FID	FID/PID	PID	ECD/AID/PID*	PID
Precision	±10%	±10%	-	-	-
Sensitivity	0.1 ppmv (benzene)	0.01 ppmv (benzene)	0.1 ppb (benzene)	0.01 ppm benzene (AID)	0.1 ppm (benzene)
Range	0.1 ppmv-1,000 ppmv	0.01-10,000 ppmv	1 ppbv-100 ppmv	3 orders of magnitude	0.1-1,000 ppm
Temperature Programming	Yes*	Yes*	No	No	No
Carrier Gas	Nitrogen	Nitrogen	Air	Argon	Air
Weight	73 lbs	25 lbs	26 lbs	40 lbs	31 lbs
Cost	$3,900	$7,300	$7,000	$13,000	$4,600
Comments	-	-	Instrument can be used as portable THC analyzer	Price includes microprocessor, recorder, and training course	-
Contact Information	(713) 370-2495	(617) 964-6690	(516) 351-5809	(201) 945-3694	(215) 268-3181

*Optional

FID and a PID which can be operated either separately or in series. The PID can be added to other instruments if there is room. The ECD is extremely sensitive and is selective for most halogenated compounds with detection limits of 1.0 ppbv with no concentration of the sample (Marrin, et al., 1984). In one study, both a cryogenic concentration step and an ECD were used to analyze trichlorofluoromethane and dichlorodifluoromethane below the 100 pptv (parts per trillion) level (Weeks, et al., 1982).

The chromatography columns chosen for field analysis depend on the types of compounds and on their volatility. A nonpolar methyl silicon liquid phase, such as SE-30, has been used extensively for hydrocarbons and halocarbons. Columns packed in stainless steel have been used more extensively for field use than those packed in glass and capillary columns. The packed columns have a higher capacity than capillary columns, and large volumes of samples can be injected without the need for cryogenic concentration steps. The lower carrier gas-flow rates of capillary columns would require almost a minute to inject a 1 mL sample and would create very broad peaks while a packed column at a typical carrier flow rate of 30 mL/min would take 2 seconds to inject 1 mL. Stainless steel is chosen over glass because it is easier to install and does not break during transport or use.

The chromatographic data can be acquired in the field on stripchart recorders, on integrators, or on a portable computer. Most of the portable GCs can be supplied with small stripchart recorders. Small integrators such as the HP 3390 can be useful to store calibration information and to integrate peak areas or heights. A portable computer with chromatographic software becomes very useful when the raw data needs to be stored, when more than one detector is being used, and when the data from different analyses or detectors needs to be compared.

Off-site laboratory instruments--When positive identification is needed, when very low detection limits are required, when difficult sample matrices are encountered, or when environmental conditions prohibit an on-site analysis, soil gas samples will have to be sent to an off-site laboratory. The off-site lab may have the instrumentation discussed above, but generally a higher sophistication of instrumentation is used.

If low detection limits are required, the samples can be collected on a solid adsorbent or in a stainless-steel canister and sent to a lab where the sample can be cryogenically concentrated. The organic components of a larger volume of soil gas can be trapped at cryogenic temperatures by using liquid oxygen, liquid argon, or dry ice/acetone baths. To trap large volumes of sample, water needs to be removed from the sample. Permapure driers, potassium carbonate (K_2CO_3) (Colenutt, et al., 1980), and magnesium dichlorate [$Mg(ClO_4)_2$] (Schmidt, 1983) have been used to remove water from air samples. Recoveries of halogenated hydrocarbons are good when these drying methods are used, but for polar compounds such as alcohols and aldehydes, variable recoveries have been found. For injection of volumes smaller than approximately 250 mL, no drying method is required. The sample is trapped on glass beads or glass wool packed in 1/8 in. stainless-steel tubing. The frozen samples are thermally desorbed by using heat cartridges and boiling water and are injected onto a column by switching a gas-sampling valve.

Adsorbent samples are injected by placing the cartridges into a block heater and thermally desorbing at a high temperature into a flow of an inert gas such as helium. Since most adsorbents do not have an affinity for water, no drying method is required. For high-resolution analysis of adsorbent samples, a second concentration step is needed to keep the desorbed effluent from "broadening" before it reaches the column. A cryogenic trap or a smaller secondary adsorbent is generally used to focus the sample before analysis.

The chromatographic separation available in the laboratory can be superior to that in the field. The use of subambient temperature programming and capillary columns allows most volatile compounds to be separated. The chromatographic condition and columns used have been described in several papers (Krost, et al., 1982; Westberg, et al., 1982; Jeltes, et al., 1977; Cox, et al., 1982; Westberg, et al., 1984). In most analyses, a non-polar methyl-silicon, fused-silica capillary column has been used. These columns can separate up to 300 different compounds. The oven temperature is usually programmed from subambient temperatures to over 100°C to separate the full range of VOC found in environmental samples.

The detection methods used for analysis of soil-gas samples include:

- Flame ionization detector (FID) for the full range of organic compounds;
- Photoionization detector (PID) for the aromatic hydrocarbons and sulfur species;
- Electron capture detection (ECD) for selective detection of halogenated hydrocarbons;
- Hall Electrolytic Conductivity detector (HECD) for the specific detection of halogenated species, nitrogen

elements containing organics, or sulfur containing species; and

- The flame photometric detector (FPD) for sulfur and phosphorus compounds.

Good reviews have been written describing the merits and limitations of these detectors (Farwell, et al., 1981; Hill, et al., 1982; Sevick, 1976). In addition to these standard GC detectors, several other configurations have been used specifically for soil gas. These include the combinations of the FID-PID-HECD described by Earp and Cox (1982) and used for soil-gas measurements by the Radian Corporation (1984, S-1984, T-1984). The combination of the FID and PID provides qualitative information to aid in the identification of hydrocarbons while the HECD can selectively detect and quantitate halogenated hydrocarbons. The multiple detector method combined with high resolution chromatography is a powerful tool providing accurate quantitation for all hydrocarbon and halogenated species with a high degree of confidence in the compound identification. Unidentified compounds can be easily classified as an alkane, alkene, aromatic, or halogenated hydrocarbon from the responses of the detector.

A new technique which has been applied to the analysis of hazardous waste is GC with Fourier transform infrared spectrometry (GC/FTIR) (Shafer, et al., 1984). The FTIR can quickly, with good sensitivity, scan the infrared spectrum of an eluting peak which can then be quantitated by using an FID or other GC detector. The infrared spectrum, after some data manipulation, can be compared to a spectral library to make identifications. A similar technique which has been used extensively in environmental analysis is GC mass spectrometry (GC/MS). A mass spectrometer is used to obtain a mass spectrum of the eluting GC peaks. A mass spectrum can sometimes make position identifications of unknown compounds, and, in the single ion mode, it is extremely sensitive and selective for the compound of interest. A good review of the GC/MS technique has been published (tenNoever, et al., 1979). The cost of these two techniques, compared to the possible benefits, has been the main factor that has limited their use in soil-gas measurements.

Conclusion--Modern analytical laboratory methods have been developed to the point where VOCs in soil gas can be separated and quantitated in the sub-ppbv concentration range, and identification can be made with a high level of confidence. The researcher's job is to determine what level of sophistication is necessary. The use of portable analyzers and field GCs to screen the sample can often provide the answers needed to make this decision. Areas where better methods are needed include the collection and determination of oxygenated compounds, of sulfur compounds, and of nitrogen containing compounds. Determinations of these compounds are difficult because of their polar nature compared to the non-polar nature of the hydrocarbons and halogenated hydrocarbons. Drastic measures are generally required to obtain a reasonably low detection limit for these compounds such as the field collection of sulfur species that makes use of the deactivated cryogenic traps described by Farwell (1979).

Quality Assurance/Quality Control (QA/QC)

For an analytical procedure to have any value, a QA/QC program must be designed so that the quality of the data is defined (i.e., confidence limits) and so that assurance exists that the method is performing at that level. Most analytical method QA/QC plans contain a calibration step, a linearity check, a QC standard analysis, a blank analysis, a duplicate analysis, and an audit sample or interlaboratory sample analysis. A typical calibration and quality control schedule for various analytical systems is given in Table 5.4. The QA/QC plan should address the sampling method, the analytical method, and the data reduction and reporting steps. The acceptance criteria chosen are limited by the available analytical and sampling techniques performance, but they should be set by the data requirements needed to make the necessary decisions. These requirements should be determined for each project during the initial Data Quality Objective planning phase of the project before any data is acquired.

Method Calibration--

Calibration methods vary depending on the instrument used and the level of confidence required. The portable organic analyzers have single calibration capabilities which limit their use when accurate values are needed. Most analyzer methods use a single component standard at several concentrations such as methane or hexane for FID and benzene for PID analyzers. Since none of the analyzer response factors are universal for VOCs, calibration procedures using a single component do not provide accurate values for the entire range of VOC compounds. The values obtained will also vary greatly in keeping with the compound that is used to calibrate the analyzer.

Calibrating GCs can be more specific, and the actual method or standard used depends on the detector. For field GCs with FIDs, a single component standard such as propane or hexane can be used to calibrate the instrument. If the VOCs can be separated into carbon number class, concentration can be calculated by assuming an equal carbon response for the FID.

TABLE 5.4. SUMMARY OF SUGGESTED CALIBRATION AND QUALITY CONTROL REQUIREMENTS FOR ANALYTICAL SYSTEMS

Type of Instrument	Type of Detector	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
Portable THC Analyzer	FID	1) Multipoint calibration (zero plus three upscale concentrations)	At start of program	Methane or other aliphatic compound	Correlation coefficient ≥0.995	Repeat multipoint calibration after checking calibration dilution system
		2) Zero/span calibration	Daily	UHP Air or N_2/methane	Response factor agreement within ±20% of mean RF for multipoint calibration	1) Repeat zero/span calibration 2) If still unacceptable, repeat multipoint calibration
		3) Control sample analysis	Daily, prior to testing	Methane	Measured concentration within ±10% of certified concentration	1) Repeat zero/span calibration 2) Repeat control sample analysis
		4) Drift check	Daily, at conclusion of testing	Methane	Drift ≤20% of the input value	1) Flag day's data as questionable 2) Repair or discontinue use of analyzer
	FID	1) Multipoint calibration (zero plus three upscale concentrations)	At start of program	Benzene or other aromatic compound	Correlation coefficient ≥0.995	Repeat multipoint calibration after checking calibration dilution system
		2) Zero/span calibration	Daily	Benzene or other aromatic compound	Response factor agreement within ±20% of mean RF for multipoint calibration	1) Repeat zero/span calibration 2) If still unacceptable, repeat multipoint calibration
		3) Control sample analysis	Daily, prior to testing	Benzene or other aromatic compound	Measured concentration within ±10% of certified concentration	1) Repeat zero/span calibration 2) Repeat control sample analysis
		4) Drift check	Daily, at conclusion of testing	Benzene or other aromatic compound	Drift ≤20% of the input value	1) Flag day's data as questionable 2) Repair or discontinue use of analyzer
Portable Gas Chromatograph	FID	1) Multipoint calibration (zero plus three upscale concentrations)	At start of program	Benzene or toluene	Correlation coefficient ≥0.995	Repeat multipoint calibration after checking calibration dilution system
		2) Zero/span calibration	Daily	UHP air or N_2/methane	Response factor agreement within ±20% of mean RF for multipoint calibration	1) Repeat zero/span calibration 2) If still unacceptable, repeat multipoint calibration
		3) Control sample analysis	Daily, prior to testing	Benzene	Measured concentration within ±10% of certified concentration	1) Repeat zero/span calibration 2) Repeat control sample analysis

(Continued)

TABLE 5.4.(continued)

Type of Instrument	Type of Detector	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
Portable Gas Chromatograph (Continued)	FID	4) Drift check	Daily, at conclusion of testing	Benzene	Drift ≤20% of the input value	1) Flag day's data as questionable 2) Repair or discontinue use of analyzer
		5) Retention time checks	Daily	Benzene or toluene	None	None
		6) Analytical blanks	Daily	UHP air or N_2	Measured concentration ≤5% of the instrument span value	Clean/replace system components until acceptable blank can be obtained
		7) Sampling system blanks	Daily (plus after very high samples)	Sample gas	Measured concentration ≤5% of the instrument span value	Clean/replace system components until acceptable blank can be obtained
		8) Duplicate samples	10% of sampling points (minimum)	Sample gas	None; provides a measure of total sampling variability	None
		9) Control point samples	After every 10 samples or once per day, whichever is greater	Sample gas	None; provides a measure of temporal variability	None
		10) Background samples	One sample per day	Sample gas	None; provides a measure of background concentration	None
	PID	1) Multipoint calibration (zero plus three upscale concentrations)	At start of program	Benzene or toluene	Correlation coefficient ≥0.995	Repeat multipoint calibration after checking calibration dilution system
		2) Zero/span calibration	Daily	UHP air or N_2/methane	Response factor agreement within ±20% of mean RF for multipoint calibration	1) Repeat zero/span calibration 2) If still unacceptable, repeat multipoint calibration
		3) Control sample analysis	Daily, prior to testing	Benzene	Measured concentration within ±10% of certified concentration	1) Repeat zero/span calibration 2) Repeat control sample analysis
		4) Drift check	Daily, at conclusion of testing	Benzene	Drift ≤20% of the input value	1) Flag day's data as questionable 2) Repair or discontinue use of analyzer

(Continued)

TABLE 5,4.(continued)

Type of Instrument	Type of Detector	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
Portable Gas Chromatograph (Continued)	PID	5) Retention time checks	Daily	Benzene or toluene	None	None
		6) Analytical blanks	Daily	UHP air or N_2	Measured concentration ≤5% of the instrument span value	Clean/replace system components until acceptable blank can be obtained
		7) Sampling system blanks	Daily (plus after very high samples)	Sample gas	Measured concentration ≤5% of the instrument span value	Clean/replace system components until acceptable blank can be obtained
		8) Duplicate samples	10% of sampling points (minimum)	Sample gas	None; provides a measure of total sampling variability	None
		9) Control point samples	After every 10 samples or once per day, whichever is greater	Sample gas	None; provides a measure of temporal variability	None
		10) Background samples	One sample per day	Sample gas	None; provides a measure of background concentration	None
Off-Site Gas Chromatograph	FID	1) Multipoint calibration (zero plus three upscale concentrations)	1/month	Propane/hexane	Correlation coefficient ≥0.995	Repeat linearity check
		2) Single point calibration check	Daily, prior to sample analyses	Propane/hexane	Response factor agreement within ±20% of most recent average RFs for multipoint calibrations	Repeat single point calibration
		3) Retention time check	Daily, prior to sample analyses	Multicomponent standard	Agreement with preestablished relative retention times	Adjust GC conditions and repeat RT check
		4) Control sample analysis	Daily, prior to sample analyses	Sample gas	1) Correct identification of 90% of components 2) For 90% of components, measured concentrations within ±30% of actual concentrations	Repeat control sample analysis

(Continued)

TABLE 5.4.(continued)

Type of Instrument	Type of Detector	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
Off-Site Gas Chromatograph (Continued)	FID	5) Duplicate analyses	Minimum of 10% of samples (all duplicate canister samples will be analyzed in duplicate)	Sample gas	CV ≤20% for ten major sample components	Repeat sample analysis
		6) Blank analysis	Daily, prior to sample analysis	UHP air or N_2	Total ≤20 ppbv-C	1) Clean system 2) Repeat blank analysis
	PID	1) Multipoint calibration (zero plus three upscale concentrations)	1/month	Propane/hexane	Correlation coefficient ≥0.995	Repeat linearity check
		2) Single point calibration check	Daily, prior to sample analyses	Propane/hexane	Response factor agreement within ±20% of most recent average RFs for multipoint calibrations	Repeat single point calibration
		3) Retention time check	Daily, prior to sample analyses	Multicomponent standard	Agreement with preestablished relative retention times	Adjust GC conditions and repeat RT check
		4) Control sample analysis	Daily, prior to sample analyses	Sample gas	1) Correct identification of 90% of components 2) For 90% of components, measured concentrations within ±30% of actual concentrations	Repeat control sample analysis
		5) Duplicate analyses	Minimum of 10% of samples (all duplicate canister samples will be analyzed in duplicate)	Sample gas	CV ≤20% for ten major sample components	Repeat sample analysis
		6) Blank analysis	Daily, prior to sample analysis	UHP air or N_2	Total ≤20 ppbv-C	1) Clean system 2) Repeat blank analysis

(Continued)

TABLE 5.4.(continued)

Type of Instrument	Type of Detector	Type of Calibration/QC Test	Frequency	Gas Standard(s)	Acceptance Criteria	Corrective Action
Off-Site Gas Chromatograph (Continued)	HECD	1) Quantitative standard	Daily, prior to sample analysis	Multicomponent standard	Response factor agreement within ±30% of three-day rolling mean RFs for all components	Repeat calibration
		2) Retention time check	Daily, prior to sample analyses	Multicomponent standard	None; will provide basis for comparison of FID/PID results to HECD results	None
		3) Control sample analysis	Daily, prior to sample analyses	Sample gas	1) Correct identification of all components 2) For 90% of components, measured concentrations within ±30% of actual concentrations	Repeat control sample analysis
		4) Duplicate analyses	Minimum of 10% samples (all duplicate canister samples will be analyzed in duplicate)	Sample gas	CV ≤20 for ten major sample components	Repeat sample analysis
		5) Blank analysis	Daily, prior to sample analyses	UHP air or N_2	Total ≤20 ppbv-C	1) Clean system 2) Repeat blank analysis

Otherwise, the concentration values are reported in the units of volume ratios of carbon (i.e., ppmv-C). For example, one ppmv of hexane would be reported as 6 ppmv-C.

Only two primary gas standard are available for GC calibration, and they are the NBS propane and benzene standards. The propane standard is available in concentrations of 1 ppm, 3ppm, 10 ppm, 50 ppm, 100 ppm, and 500 ppm. All other standards can be certified by using the NBS propane standard. These standards have been found to be very stable even at the 1 ppm level.

The PID detector is much more difficult to calibrate because the response factors vary more than those observed for the FID for each compound. To accurately quantitate samples, a response factor for each component of interest would be required. In most cases, a single compound such as benzene is used to calibrate the response. If a known mixture of organic compounds is being monitored, such as that found in a gasoline spill, the mixture can be used to calibrate the instrument and to provide a number quantitating the total amount of that mixture in a given sample. This works well if the composition at the site is homogeneous and if there are no other significant sources of the compounds in the mixture. Dr. Tom Spittler of the U.S. EPA Region 1 calibrates a PID for gasoline by analyzing the headspace above known amounts of gasoline dissolved in water (Clark, et al., 1983). Working level standards are prepared according to the procedures in EPA Method 624 (US EPA, 1982). The dilute (e.g., 40 ppb) gasoline-in-water standards are stored under liquid mercury in serum vials. When needed, air is introduced into the vial, and a headspace sample is collected. This can also be used as a qualitative check for matching retention times and for fingerprinting the sample with the source.

Once the instrument is calibrated, a quality control standard should be analyzed which comes close to approximating the expected concentration and matrix of the samples. This sample is a check to see if the calibration will accurately provide a concentration value for the components of interest. For the FID, a mixture of components is analyzed by using the single component response factor to see if it can accurately identify and quantitate the components within a set limit. This QC standard analysis provides a good indication of the day-to-day variability of the instrument.

Duplicate analyses and samples are required to determine the variability of the sampling and analytical technique. Nested duplicate samples, where samples are collected in duplicate and analyzed in duplicate, provide a means to statistically determine total variance of the method and the amount of variance which results from both the analytical method and the sampling method.

Blank analyses are required to determine the level of contamination which results from the sampling and analytical methods. Field blanks are generated by passing a gas from a clean source through the sampling apparatus and collecting it by the method being used. This sample is sent to the lab and is analyzed as if it were a real sample. Contamination because of the analytical system is determined by injecting a volume of clean air or nitrogen into the instrument. Blanks should be run periodically and analytical system blanks run between the analysis of high-level samples and low-level samples.

To determine the absolute accuracy and lab-to-lab variability, audit sample analyses and interlaboratory comparison studies are required. Performance audit samples are unknown samples provided by one lab and submitted to another lab to be analyzed simultaneously with the soil-gas samples. Interlaboratory comparisons consist of collecting a large sample, dividing that large sample into smaller samples, sending them to several labs for analysis, and comparing the results. Audit samples have not been developed specifically for soil-gas measurements; however, the EPA has established an extensive repository of organic gaseous compounds at a wide range of concentrations to be used as audit materials for emissions analysis (Jayanty, et al., 1983). There are no published results for interlaboratory comparison for soil-gas analysis; however, many of the same techniques have been compared for the analysis of ambient air (Balfour, et al., 1984). The results of this study of five laboratories using the same method (GC/FID) with differing analytical procedures showed a coefficient of variance of 11 percent in the value of total nonmethane hydrocarbons.

Conclusions--

The level of QA/QC effort required depends on the data accuracy and precision requirements. In any case, the QA/QC program should establish the limits of both the sample collection and analysis methods and should ensure that they continue to perform within these limits. Accurate calibration methods for portable analyzers have not been developed, and calibration of a large number of compounds for PID, ECD, and MS is difficult. There is a need for standard reference material for VOCs in soil as well as accurate QC standards and interlaboratory comparison studies.

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CHAPTER 6

STATISTICAL TREATMENT OF SOIL ORGANIC VAPOR MEASUREMENTS

INTRODUCTION

Soil organic vapor (SOV) measurement is usually performed in an exploration phase of an investigation. The statistician has two duties at the start of such an investigation. They are (i) to determine a method for taking the measurements in such a way as to meet requirements for data precision in a realistic and cost effective manner, and (ii) to help determine the locations for the initial exploratory survey in accordance with prior knowledge about the site and the objectives and budget of the project. The determination of the precision of the measurements and the size of the contributions of various sources of error is the starting point in the planning of all good sample surveys. The measurements must represent the SOV concentrations in the soil at the sites where the samples are taken. The measurements will be worthless if they merely represent the errors generated in obtaining, handling, and analyzing the samples. One should not wait till the end of a survey to determine the precision of the measurements, for then it may be too late to save the study from bad data. Obviously it is impossible to completely eliminate errors. However, by use of proper statistical techniques, it is possible to measure the effects of the various sources of error on the precision of the measurements and, if necessary, to find the most economical means for reducing the effects so as to attain a desired level of precision.

The proper methods for choice of locations for the taking of measurements is unique to each site because of the changes in objectives, budgets, and prior knowledge between sites. The decision concerning location of sample points must be made in concert with the other principal participants in the study and, because of the exploratory nature of the SOV investigations, may in large part be subjective. Some words of advice on possible sampling patterns have been given in a preceding chapter.

Techniques for assessing measurement precision and contributions of various sources of error to total error are discussed in this chapter along with some comments on the use of the final survey data in interpolation and contouring procedures.

COMPONENTS OF VARIANCE ANALYSIS

The central statistical procedure involved in the process of measuring and improving precision is called components of variance analysis. This procedure is based on a model for the measurements that includes an equation of the form,

$$Y_i = \mu_i + \varepsilon_{i1} + \varepsilon_{i2} + \ldots + \varepsilon_{ik}$$

where Y_i is a measurement of the concentration of an organic vapor in sample i, μ_i is the expected value of such a measurement (i.e., the average of a hypothetical population of repeated measurements on samples taken at the same location and using the same technique), and ε_{ij} is the error in the measurement coming from source j (j=1,...,k). The measurements are said to be precise if the sum of the ε's on the right-hand-side of the equation is near zero with high probability. Hence, to obtain precise measurements, one wants the contributions ε_{ij} from each of the various sources of error to be small with high probability.

To develop the above model equation, one must be sufficiently familiar with the sample acquisition, handling, and analysis process to search out and list all the major sources of error. Since the size of errors vary from sample to sample and cause variation in measurements, it is common to refer to sources of error as sources of error variation or sources of variation. For example, analytical errors cause variation between analyses of subsamples of a sample of soil gas. If one considers soil organic vapor measurements taken by drawing soil gas into a soil probe, withdrawing gas from the probe with a syringe and finally inserting the gas from the syringe into a gas chromatograph for measurement of a chemical concentration, then the variation in gas chromatograph measurements of gas from several syringes taken from the same probe after a single purge and relaxation of vacuum would represent the variation caused by such things as air leakage into the syringes and analytical errors in the gas chromatography. If several syringes of gas are withdrawn from each of several closely spaced probes at a sampling location, the variation of the average measurements for the probes would give information concerning combined variation caused by short range spatial differences in concentrations of the SOV being measured, by differences in insertion of probes, by differences in the vacuum achieved in the purging of the probes, and perhaps by leakage of surface air into the probes. It is wise to determine the sizes of the contributions of the various sources of error variation to the total variability of the data prior to the investigation of the spatial distribution of the SOV. Knowledge of the contribution of the sources of variation allows the investigator to determine how best to allocate resources to obtain precise estimates of SOV concentrations (or perhaps to determine that the study will not be able to obtain desired levels of precision and therefore should not be completed). For example, if there is a large irregular variation between measurements at the same sampling location taken at substantially different times (say a week apart), the investigator will have to determine whether this variation is due to differences in measurement procedures or is due to changes in environmental conditions such as ambient temperature and atmospheric pressure. If the cause is change in measurement procedures, this variation might be substantially reduced by additional training and practice. If the cause of the large variation over time is due to environmental factors, it may be necessary to establish one or more control sites and to measure at the control sites whenever measurements are taken at other sites. This would provide the information needed to make measurements taken at different times comparable.

As is implied by its name, the components of variance technique uses variance (the second moment about the mean) as the measure of the variation caused by errors. If the probability distribution of the errors is normal (Gaussian) as is assumed in variance components analysis (the error terms are assumed to be independent random variables with ε_{ij} having normal distribution with mean zero and unknown variance σ_j^2), the shape and spread of the distribution is completely determined by the variance. Under the assumption of a normal distribution for Y_i, the precision of the measurement is measured by its variance; the smaller the variance, the better the precision. However, for most other types of probability distributions, variance does not completely characterize the spread of the distribution. In addition, for many nonnormal distributions, the spread of the distribution changes as the mean, μ_i, changes. It is impossible to estimate variances of the ε_{ij} if the variances are not constant (i.e., if they change with the magnitudes of the measured concentrations). Hence, if variances change as the mean changes, it is vital that the data be transformed in such a way as to stabilize variances relative to the mean. Typically, if one can stabilize the variance with a transformation, that transformation also makes the distribution more symmetric (see Section 4F of Hoaglin et al., 1983), and thereby a better approximation to the normal. A frequently used variance-stabilizing transformation for data

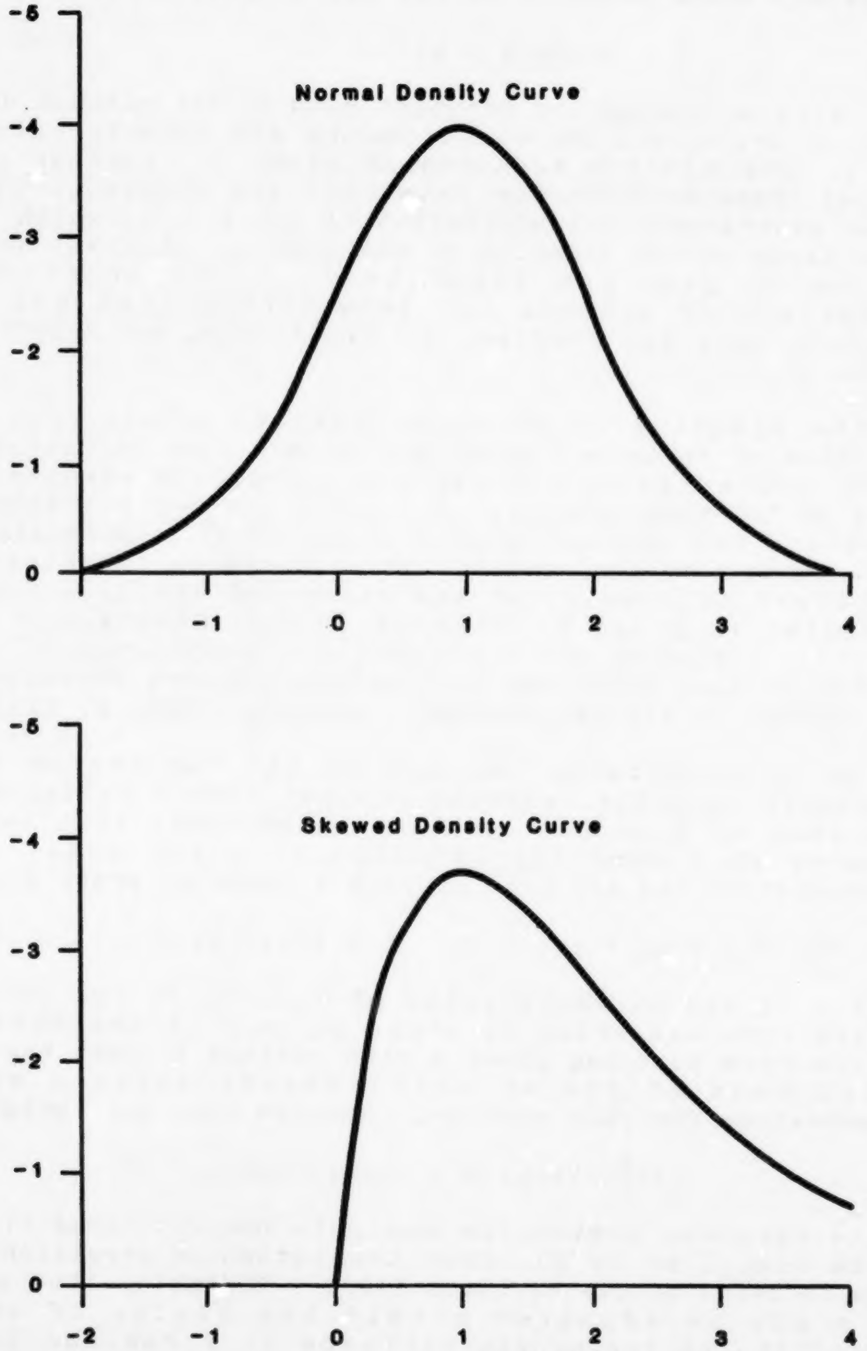

Figure 6.1. Density curves for normal and skewed distribution.

from distributions that are skewed to the right is the logarithmic transformation of the measurement Z into Y with

$$Y = \log(Z + m)$$

where m is a nonnegative constant such as the minimum detection limit, 1, or, if all the measurements are considerably larger than 1, the minimum measurement minus 1. Another commonly employed transformation for data that are skewed to the right is the square-root transformation (i.e., $X = \sqrt{Z}$) which does not reduce large values relative to the smaller observations quite as much as does the logarithmic transformation. For discussions of methods for determining when and how to transform data see Hoaglin, et al. (1983), and Scheffe (1959, Section 10.7).

The planning of an experiment to obtain data for the estimation of variance components is very much dependent on the nature and costs of the various operations involved in the taking of SOV measurements. A review and bibliography of the literature for the design and analysis of experiments planned for variance component estimation is given by Anderson (1975). A detailed discussion of the theory of variance components estimation is given in Scheffe (1959, Chapters 7 and 8). Computer programs are available for components of variance analysis in most mainframe statistical software packages (e.g., PROC VARCOMP in the SAS package - see Ray, 1982, p. 223).

As an example of the use of the results of variance components analysis, suppose one can take k syringes of gas from each of m probes located on the nodes of a small grid centered on a sampling location. If the model for the measurement of the gas from syringe i taken at probe h is

$$Y_{hi} = \mu + \varepsilon_h + \varepsilon_{hi} \qquad h = 1,\ldots,m;\ i = 1,\ldots,h,$$

where μ is the expected value of Y_{hi}, ε_h is the error which results from measuring at probe h, ε_{hi} is the error which results from sampling probe h with syringe i, then the variance of the mean of the km measurements gives a measured concentration for this sampling location that has variance

$$V(\bar{Y}) = V(\varepsilon_h)/m + V(\varepsilon_{hi})/(mk).$$

If the variance components analysis has estimated $V(\varepsilon_h)$ to be 10 and $V(\varepsilon_{hi})$ to be 20, then the estimated precision of $\bar{Y}$ is given in terms of the variance $(10/m + 20/(mk))$. The numbers k and m may be adjusted within the limits of costs and feasibility to reduce the variance to a desired level and thereby to increase the precision of the measured concentration obtained from each sampling location. For $m=1$ and $k=4$, $V(\bar{Y})$

is estimated to be 15 which is also obtained for $m=2$ and $k=1$. If the cost of a probe is about the same as the cost of the analysis of a sample, the second option would be preferable to obtain a desired variance of 15. The second option might be essential if it is not feasible to take k as large as 4.

Variance Components Analysis Example

In this section, data from the Case Study 2.0, hereafter called the Pittman Case Study, of the chapter on case studies that follows, will be used to illustrate some of the points that were made concerning variance components analysis that was made above. The study was run to test an SOV sampling procedure by comparing its results with data obtained from nearby wells. The SOV data consist of gas chromatograph measurements of chloroform concentrations (in ppbv) in gas obtained in 250 µl syringes from probes. Although no special experiment was performed to measure variance components, this study does provide data from which some variance components may be estimated.

The first step in a variance components analysis of this data is a search for an appropriate transform of the data to move it toward normal distribution characteristics. Table 6.1 is obtained from the data in Table 6.2 of the Pittman Case Study by ordering the 23 sets of replicate analyses according to the size of their sample means. In Table 6.1, the standard deviations of log transformations and of square-root transformations of the sample data are given along with the standard deviations for the raw data provided in Table 6.2. If one looks at the standard deviations of the raw data for the smallest 8 means and for the largest 8 means, it is obvious that the sample standard deviations are increasing along with the means. If one does the same thing for the standard deviations of the log-transformed data, one finds that the standard deviations are getting smaller as the sample mean increases which implies that the transformation has over compensated for the skewed distribution. Finally, when one checks the first and last 8 standard deviations for the square-root transformed data, one finds no evidence of trend of the sample standard deviations with the sample means. Hence, in this case, the square-root transformation seems a reasonable choice.

The analytical (between syringes) error variance for the square-root transformed chloroform measurements of the Pittman Case Study may now be estimated with the pooled estimator of the variance,

$$s_p^2=\Sigma(n_i-1)s_{x_i}^2/\Sigma(n_i-1)$$

where s_{xi}^2 is the sample variance calculated from the n_i square-root transformed measurements taken at location i ($i=1,\ldots,23$). From the square-root transformations of the data in Table 6.2, one finds $s_p^2=0.0836$ and $s_p=0.29$ (based on 43 degrees of freedom).

In the case study, measurements were taken after each of a series of purges of the same probe. These measurements allow estimation of "between-purge" variance. Two syringes were loaded with gas after each of four purges of the probe. The results of the analyses of the gas in the syringes are given in Table 6.2. The usual model for the analysis of the transformed measurements is

$$X_{ij} = \mu + \rho_i + \epsilon_{ij}$$

where μ is the mean, ρ_i is a random variable representing the deviation associated with following purge i and is distributed $N(0,\sigma_p^2)$, ϵ_{ij} is the random variable representing effect of syringe (analytical error) j taken after purge i and is distributed $N(0,\sigma_a^2)$, and the random variables are independent of one another. (There is some doubt concerning the independence and identical distribution of these measurements in that vacuums achieved declined from purge to succeeding purge. Perhaps it is impossible to obtain a true between purge variance estimate because of this problem.) The analysis of variance of the transformed purge data gave a mean square for analytical error of 0.13 based on 4 degrees of freedom. This estimate of σ_a^2 is remarkably close, considering the small number of degrees of freedom, to the value 0.0836 obtained earlier. The between purges mean square is 0.33, based on 3 degrees of freedom. Since the expected value of this mean square under the above model is $\sigma_a^2+2\sigma_p^2$, the estimate of the between purges component of variance would be

$$s_p^2=(0.33-0.13)/2=0.10,$$

or, when the more precise estimate of σ_a^2 found earlier is used

$$s_p^2=(0.33-0.08)/2=0.12.$$

The problem with vacuum and the small number of degrees of freedom available for between-purges-component estimation should make one suspicious of the accuracy of either estimate, s_p^2.

The extreme variability of the estimator s^2 of a variance σ^2 based on small numbers of degrees of freedom is seldom adequately appreciated. Table 6.3 indicates how the length of confidence intervals for σ^2 based on estimates s^2 varies with

TABLE 6.1. SAMPLE STANDARD DEVIATIONS FOR RAW AND TRANSFORMED CHLOROFORM MEASUREMENTS ORDERED BY SIZE OF SAMPLE MEAN

(Z = Chloroform measurement, $Y = \log(Z)$, $X = \sqrt{Z}$)

Rank	Sample Mean	Sample Size	s_Z	s_Y	s_X
1	5	3	0	0	0
2	6	2	3	0.49	0.59
3	10	3	2	0.19	0.31
4	10.5	3	0.3	0.06	0.09
5	12.3	3	0.5	0.04	0.06
6	25	3	2	0.09	0.22
7	27	3	5	0.17	0.46
8	27	3	2	0.07	0.20
9	27	3	5	0.20	0.53
10	28	3	5	0.18	0.45
11	30	3	1	0.03	0.09
12	32.1	2	0.2	0.01	0.02
13	45.6	3	0.2	0.01	0.02
14	55	3	2	0.03	0.12
15	72.9	3	0.1	0.00	0.01
16	112	3	12	0.11	0.55
17	115	3	6	0.05	0.28
18	161	3	6	0.03	0.22
19	171	2	0	0	0
20	266	3	6	0.02	0.17
21	326	3	10	0.03	0.29
22	376	3	6	0.02	0.15
23	511	3	17	0.03	0.37

(Kerfoot, 1985)

TABLE 6.2. CHLOROFORM CONCENTRATIONS (ppbv) MEASURED ON GASES DRAWN AFTER EACH OF A SERIES OF PURGES OF THE SAME PROBE

		Syringe 1	Syringe 2
Purge	1	10.7(3.271)*	16.4(4.050)
	2	6.6(2.569)	8.5(2.915)
	3	10.5(3.240)	9.8(3.130)
	4	10.0(3.162)	6.7(2.588)

(Kerfoot, 1985)

degrees of freedom. The table is based on an assumption of normally distributed data whereas real (and even transformed) data are nonnormal, and usually the variability of the estimator s^2 is even greater than that indicated by the table.

Also note the rapidly diminishing rate of decrease in confidence interval lengths once the number of degrees of freedom exceeds 20. This makes 20 degrees of freedom a reasonable goal in planning an experiment to estimate a variance.

TABLE 6.3. CONFIDENCE INTERVALS FOR σ^2 BASED NON s^2 AS A FUNCTION OF DEGREES OF FREEDOM (D.F.) AND ASSUMING A NORMAL DISTRIBUTION FOR DATA

D.F.	95% CONFIDENCE INTERVAL
2	$0.27s^2 \leq \sigma^2 \leq 39.21s^2$
3	$0.32s^2 \leq \sigma^2 \leq 13.89s^2$
10	$0.49s^2 \leq \sigma^2 \leq 3.08s^2$
20	$0.58s^2 \leq \sigma^2 \leq 2.08s^2$
30	$0.64s^2 \leq \sigma^2 \leq 1.78s^2$
50	$0.70s^2 \leq \sigma^2 \leq 1.61s^2$
100	$0.77s^2 \leq \sigma^2 \leq 1.35s^2$

It is important to estimate the between-probe variation of the measurements to determine how well an individual measurement characterizes the concentration of the organic vapor in the immediate vicinity of the sampling point. In the Pittman study, several probes were placed at locations only a few feet apart near well No. 627 (see Figure 7.26 of the case study). The results from the three locations (E23; E23, S3; and E20, S3) are employed to obtain an estimate of spatial variation. The model employed is:

$$X_{ij}=\mu+\lambda_i+\rho_{ij}+\varepsilon_{ij}$$

where λ_i is a random variable with a $N(0,\sigma_L^2)$ distribution representing the effect of location i, ρ_{ij} is a random variable with a $N(0,\sigma_p^2)$ distribution representing the random effect of purge j within location i, and the ε_{ij} is defined as in the previous model. The random variables are assumed to be independent. The mean square for error in the analysis of variance of the square-root transformed data is 0.182 and is an estimate of $(\sigma_p^2+\sigma_a^2)$ based on 6 degrees of freedom. This estimate agrees surprisingly well with the previous estimates for the sum of the two variances. The mean square for between locations is 21.036 and represents an estimate of $(\sigma_p^2+\sigma_a^2)+3\sigma_L^2$. Hence the estimate of σ_L^2 is (21.036-.182)/3 = 6.95. This estimate is based on only two degrees of freedom and is extremely unreliable. In addition, the investigators in the Pittman study believe that the variation observed in the data from the three probes was primarily due to the time delays in getting the samples analyzed rather than being due to short-range spatial variation in chloroform concentrations. If the estimate had been a more reliable estimate of short-range spatial variation, it would indicate that to improve the estimated concentration at a sample point significantly, one must average measurements over the results from several closely spaced (but non-interfering) probes at that location. Based on the variance components model given above, the variance of the average of the measurements on s syringes from each of m purges from each of n closely spaced probes at a sample location is given by the formula,

$$\mathrm{Var}(\bar{X}) = \sigma_L^2/n + \sigma_p^2/mn + \sigma_a^2/mns$$

When variance between probes is the major source of variation, as it is in this case, the only way to substantially reduce the variance of the mean $\bar{X}$ is to increase the number, n, of probes. When variance between purges is the major source of variation, one may increase m or n, and the choice could be made on the basis of costs. Similarly, when analytical error is the major source, one could choose on the basis of cost to increase m, n, or s, in order to decrease the variance of $\bar{X}$.

Once again it should be pointed out that the above discussion of the components of variance analysis of the Pittman data is an illustration of procedure. In actual practice, one should note that the measurements of samples from different purges of the same probe are neither independent nor identically distributed. Therefore, one should use only the sample from after the first purge in measuring concentrations. This effectively removes "between purges" as an estimable variance component. For each possible variance component, it is necessary to consider whether the assumptions of variance components analysis are reasonable. In addition, as was done above, it is necessary to decide or to investigate further the causes of large variance components (i.e., was the large between probe variance due to short-range spatial variation or differences in times the gas waited in syringes before analysis).

INTERPOLATION AND CONCENTRATION CONTOURING

One of the principal reasons for taking SOV measurements is to estimate the location of a pollutant plume. Another reason may be to indicate a possible source for a pollutant plume. Data analyses used to further these objectives usually involve interpolation between sample points and the drawing of concentration contours (isopleths). Before discussing these analyses, it is important to point out a few things about the data. SOV measurements are measurements of concentrations of certain gaseous chemical compounds near the surface. They do not necessarily represent the concentrations (or some monotone transformation of those concentrations) of the compounds directly below the sample points at the level of the plume. A positive SOV measurement at a sampling location may be a false positive (i.e., the plume does not extend below the sampling point) in that the positive measurement may be due to lateral movement in the earth of the gas from the plume around a lens of impermeable clay or rock, or it may be caused by errors in the sampling and analysis. A "none-detected" measurement may be a false negative (i.e., plume is below sampling point) caused by an impermeable layer between plume and sampling device, by biodegradation of the compound, by slow transport rate, or by sampling and measurement error. Thus a very irregular spatial pattern of SOV measurements may be due to one or more of several causes. Even a fairly regular spatial pattern of SOV measurements may not be indicative of the actual location of the pollutant plume because of lateral drift of the vapor. Under the very best of circumstances, the SOV measurements represent some monotone transformation distorted by measurement errors of the concentrations of the compounds below the sampling points at the level of the plume.

There are many methods of interpolation available to the investigator such as linear, inverse squared distance, splines, and kriging. Most such methods, such as the first three mentioned above, are deterministic (i.e., do not rely on a probability model) while some, usually denoted as kriging, do depend on probability models. Typically the various common interpolation procedures give similar results concerning the general pattern of SOV concentrations. The advantage of kriging (basically a regression procedure that uses information about the spatial correlation of observations) is that it also provides an estimated standard error for each interpolation. However, that estimated standard error is highly dependent on the probability model (commonly referred to as the spatial structure model in geostatistics). The probability model must be estimated anew for each SOV study because of the unique characteristics of different sites. Good estimation of a model requires more and better data than are usually obtained in an SOV study. For this reason, it seems better to use a simple spline or inverse-square interpolation procedure, and if an indication of the amount of error that may be involved in the interpolation is desired, cross-validation techniques (see Efron, 1982, Chapter 7) may be employed.

Finally, care must be taken in the use of computer interpolation and contouring packages so as not to obtain misleading contours. A typical situation in which misleading contours occur is one in which an observation is several orders of magnitude larger than those obtained at neighboring points (see Figure 6.2). In this case there will usually be several contour lines circling the point with the large observation; the locations of these contours reflect almost nothing other than the idiosyncrasies of the contouring package. It would be better to remove these circling contours and merely flag the large observation.

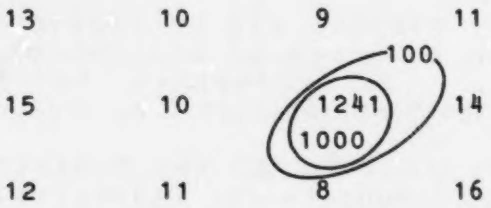

Figure 6.2. Misleading contours.

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CHAPTER 7

CASE STUDIES

INTRODUCTION

Volatile compounds are components in ground-water contamination at many, if not most, Superfund sites. Soil vapor concentration serves as a surrogate for actual measurements of the concentrations of the compounds of interest in ground-water. The usual objective in measuring organic vapors in soil is to map the lateral extent of soil and ground-water contamination or both while at the same time minimizing the number of conventional monitoring wells which must be drilled. Maps of soil vapor concentrations can be used to site ground-water monitoring wells more efficiently.

The basic approach in a soil-gas investigation at a particular site is simple in concept. The vertical profiles of organic vapors present in the soil pore spaces are measured and plotted for several locations at the site. Selection of tracer gases for the site is aided when prior information on contaminant concentrations in ground-water is available. Based on the vertical profiles, the particular organic soil gases present, and the sampling and analytical methodologies available, one or more tracer gases are selected. A sampling depth is also selected, based on the measured vertical profiles, which is expected to produce soil gas concentrations well above the minimum concentrations detectable with the analytical techniques at hand. By using this constant sampling depth, soil gas samples are collected and measured across the site preferably on a regular grid pattern. These values are then plotted on a map and are contoured either by hand or with a computer algorithm. The desired result is a contour plot of soil-gas concentrations at a constant depth across the site; the investigator hopes that this plot is related in a more or less linear way to contaminant concentrations in ground-water or in the buried waste stratum of interest.

Two case studies are presented as illustrations of this basic approach. While neither case is a Superfund site, the techniques used are very similar to investigations which might be carried out as part of a Superfund Remedial Investigation Feasibility Study. The first case study illustrates the use of soil-gas measurements as a means of delineating a plume of gasoline from a leaking underground storage tank at a rural service station. In the second case study, soil-gas measurements are used to examine the extent of ground-water contamination originating from surface impoundments and underground storage tanks at a large industrial plant.

HYDROCARBON PLUME DETECTION AT STOVEPIPE WELLS, CALIFORNIA

Gasoline Plume History

In May 1979 the odor of gasoline was detected in an unused well near a Chevron service station adjacent to the Stovepipe Wells Hotel in Death Valley National Monument. The location of Stovepipe Wells (La Brecque, et al., 1984) is shown on Figure 7.1; Figure 7.2 shows the location of the service station and hotel complex. A sample collected from the well showed that a layer of gasoline had accumulated on the water table. Service station records indicated that between October 7, 1978, and September 4, 1979, as much as 19,000 gallons of unleaded gasoline were lost. No records were available prior to October 7, 1978, but there was evidence that the buried storage tank was already leaking at that time. The total product lost was probably considerably in excess of 20,000 gallons. The National Park Service requested that the USGS assess the spreading and the hydrologic effects of the gasoline leak on the ground-water system.

The USGS drilled several wells in May, 1980; Figure 7.2 summarizes the USGS results. In 1980 well K3 contained sediments saturated with gasoline, but well J6 contained no detectable gasoline. By fall 1983, a strong gasoline odor was detected in well J6, indicating that the gasoline had continued to migrate eastward. There was considerable question as to the exact direction of the flow of gasoline, its width, and its areal extent.

Hydrogeologic Setting

The Stovepipe Wells study area is located on north-dipping alluvial-fan sediments. Ground-water is the only local source of water available to the Stovepipe Wells Hotel and associated facilities. The local aquifer consists of unconsolidated, gravelly, sandy silt having a transmissivity of about 315 m^2/d. Depth to water ranges from about 25 feet just north of the hotel to about 145 feet at a supply well up the alluvial west of the hotel. Direction of ground-water flow in the vicinity of the hotel is to the east; the regional water table appears to have declined slightly between 1977 and 1978.

Ground-water quality in the vicinity of the hotel varied from 5250 mg/l to 8790 mg/l total dissolved solids (TDS) in June 1980. TDS consists primarily of sodium, chloride, and sulfate, with high concentrations of boron and iron.

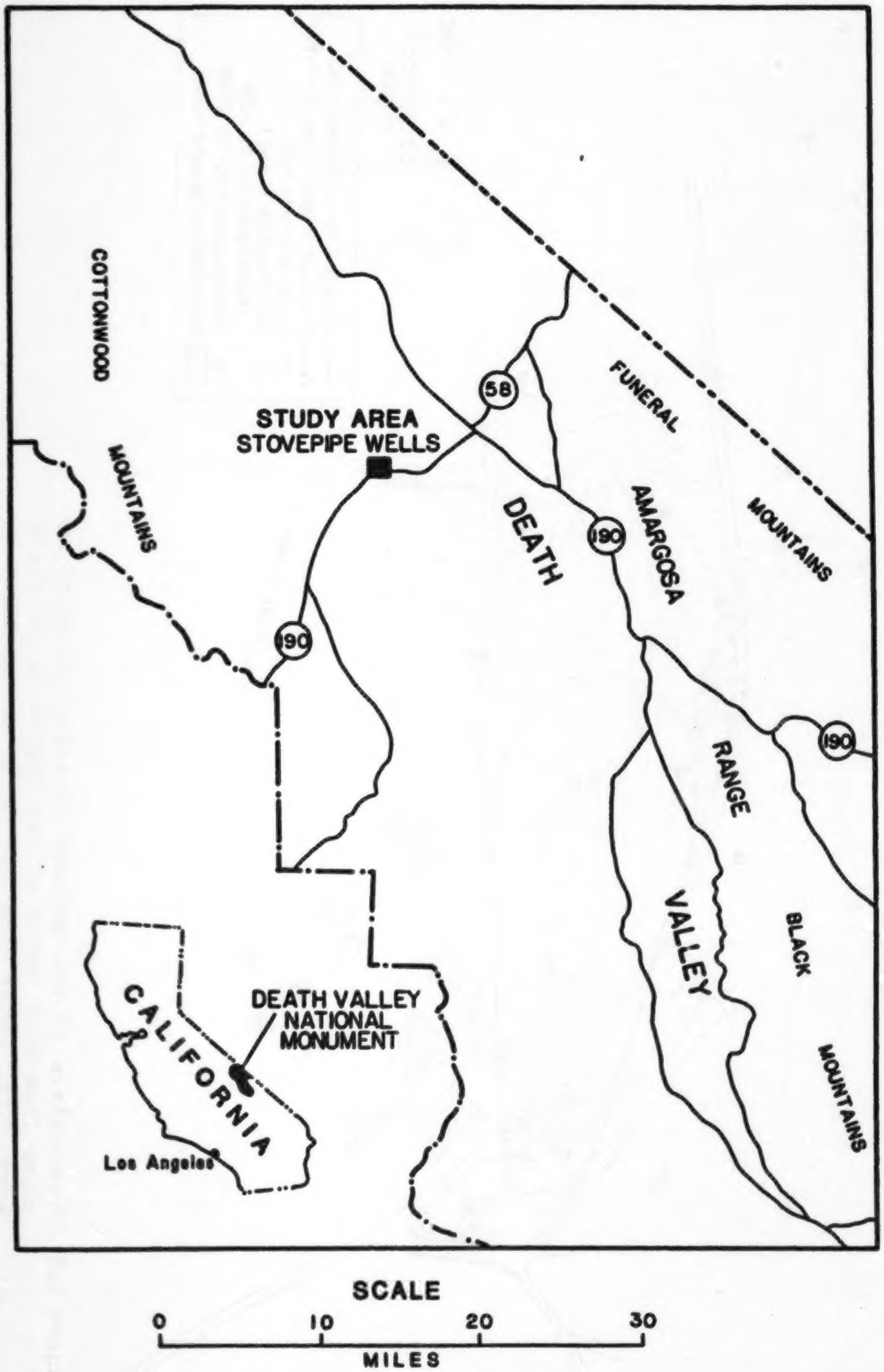

COTTONWOOD
MOUNTAINS
STUDY AREA
STOVEPIPE WELLS
58
190
190
190
DEATH
VALLEY
AMARGOSA
RANGE
FUNERAL
MOUNTAINS
BLACK
MOUNTAINS
CALIFORNIA
DEATH VALLEY
NATIONAL
MONUMENT
Los Angeles
SCALE
0
10
20
30
MILES

Figure 7.1. Location of study area.

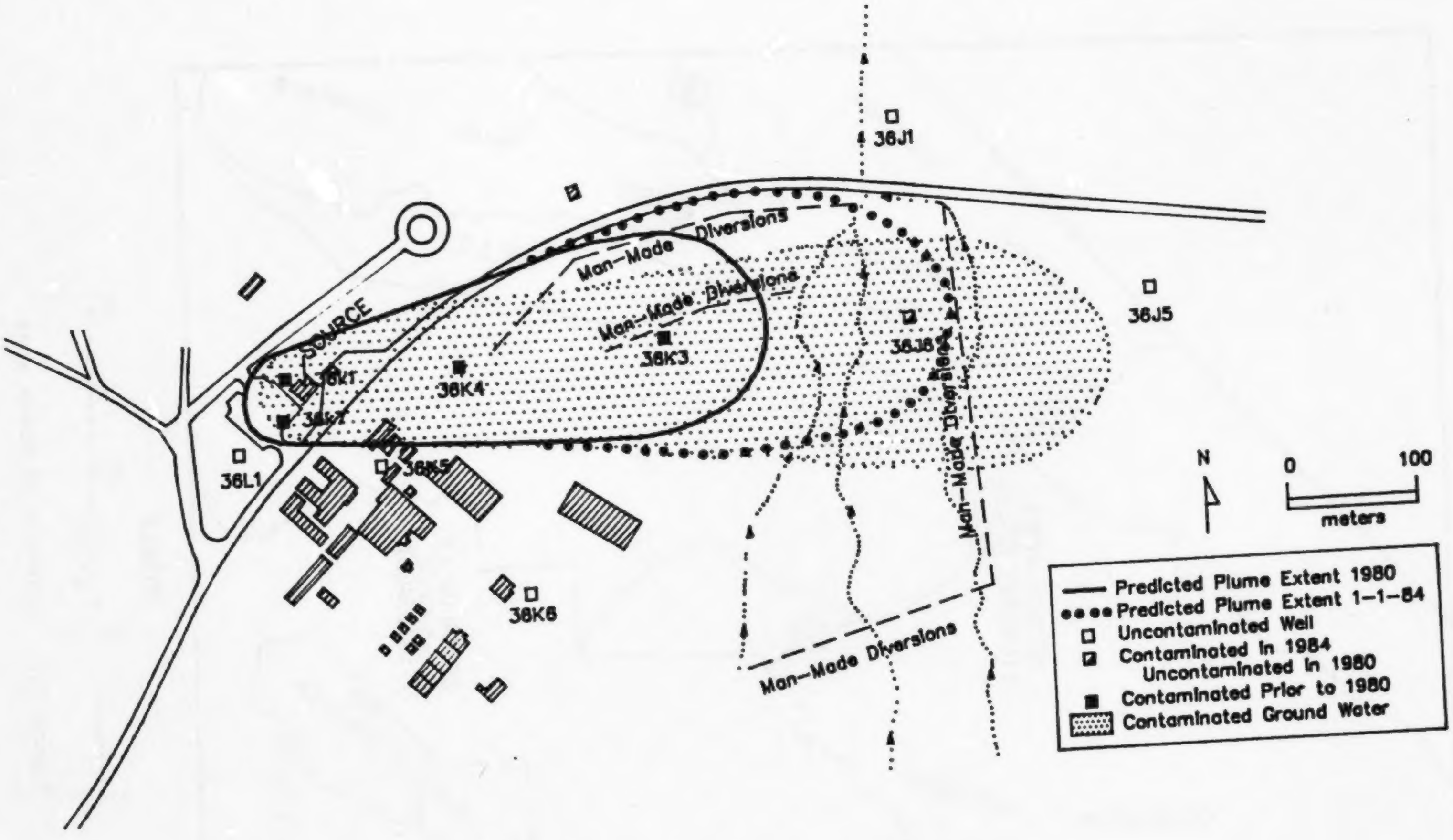

36J1
SOURCE
36K4
36K3
36J8
36J5
36L1
36K5
36K6
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
N
0
100
meters
—— Predicted Plume Extent 1980
●●●● Predicted Plume Extent 1-1-84
□ Uncontaminated Well
◪ Contaminated In 1984 Uncontaminated In 1980
■ Contaminated Prior to 1980
▨ Contaminated Ground Water

Figure 7.2. Comparison of the assumed location of gasoline plume from USGS wells at the beginning of field work (May, 1980) with the plume extent shown by subsequent Lockheed wells.

Soil Gas Measurements

Concentrations of organic vapors in soil at a depth of approximately 5 feet were mapped with a system which involved driven steel probes, a special sampling manifold, gas sample collection with a syringe, and field analysis via a field gas chromatograph with a photoionization detector. The probe, shown in Figure 7.3, was about 98 inches in length with an outside diameter of 3/4 - inch and an inside diameter of 1/4 - inch; the shaft was constructed of 4130 carbon steel. The probe tip was a cylinder of 316 stainless steel, 0.87 inches long, with a nose tapered at 30 degrees. Six ports were spaced radially around the circumference of the cylinder. Frits - porous stainless steel discs measuring 3-mm diameter by 3-mm thick - were pressed into the ports to serve as screens. Pore size was 20 microns, chosen to allow soil vapor passage while excluding most soil particles. A length of 3 mm OD Teflon tubing was connected to the ports in the probe tip; the probe was completed by threading the 3 mm Teflon tube through the probe shaft. [NOTE: Teflon is no longer recommended for soil-gas sampling because some hydrocarbons tend to adsorb or diffuse into the material. The LGAS probe used in the following Pittman, Nevada, case study used stainless steel.]

Modified fence-post drivers were used both to insert and to remove the probe from the ground. The driver was a 2.5 -inch OD cylinder with a 1.5 - inch ID. The driver and extractor are shown in Figure 7.4. Insertion of the probe was difficult at Stovepipe Wells because much of the site was covered by cobble- and boulder-bearing sands and gravels. To reduce the wear and tear on the sampling probe, a 1.25 - inch steel rod was first driven through most of the sampling depth, then removed so that the probe could be driven to the desired depth. After extraction, the soil probe cone was removed for cleaning. A clean cone was then reinstalled and used to sample the next location.

At a chosen sampling location, the probe was driven into the ground to the desired sampling depth (about 5 feet at Stovepipe Wells), the fence post driver and steel drive cap were removed, and the free end of the 3-mm Teflon tube was attached to the sample port of the gas sample collection manifold as shown in Figure 7.5. The manifold was a 3-way T-connector which connected the sample port to a Mininert valve and a shut-off valve which in turn was connected to a Mine Safety Appliances (MSA) Samplair manual pump. To obtain a sample, the shut-off valve was opened and a 75-ml volume of gas was purged from the probe with the pump. A gas chromatograph syringe was then used to extract a sample for analysis through the Mininert valve; syringes were tagged and immediately analyzed.

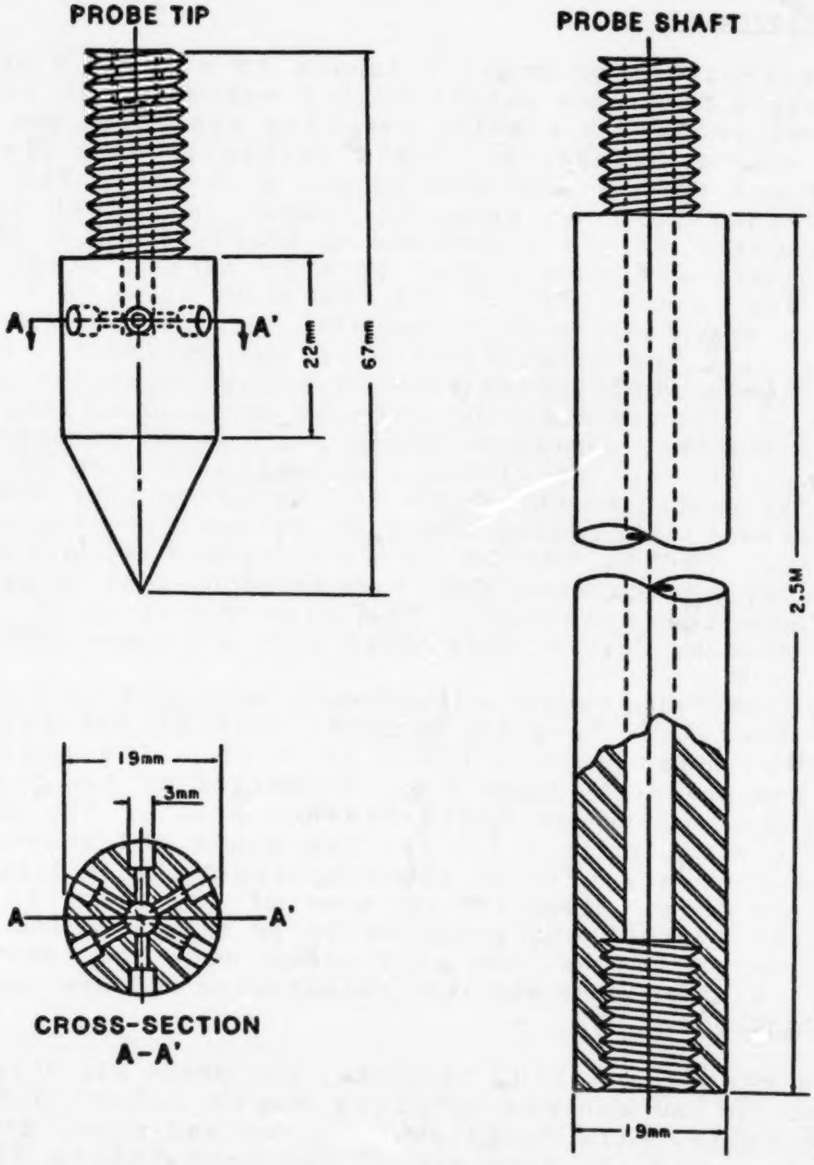

PROBE TIP
PROBE SHAFT
A
A'
22mm
67mm
2.5M
19mm
3mm
A
A'
CROSS-SECTION
A-A'
19mm

Figure 7.3. Diagram of Lockheed-EMSCO SOV probe tip and shaft.

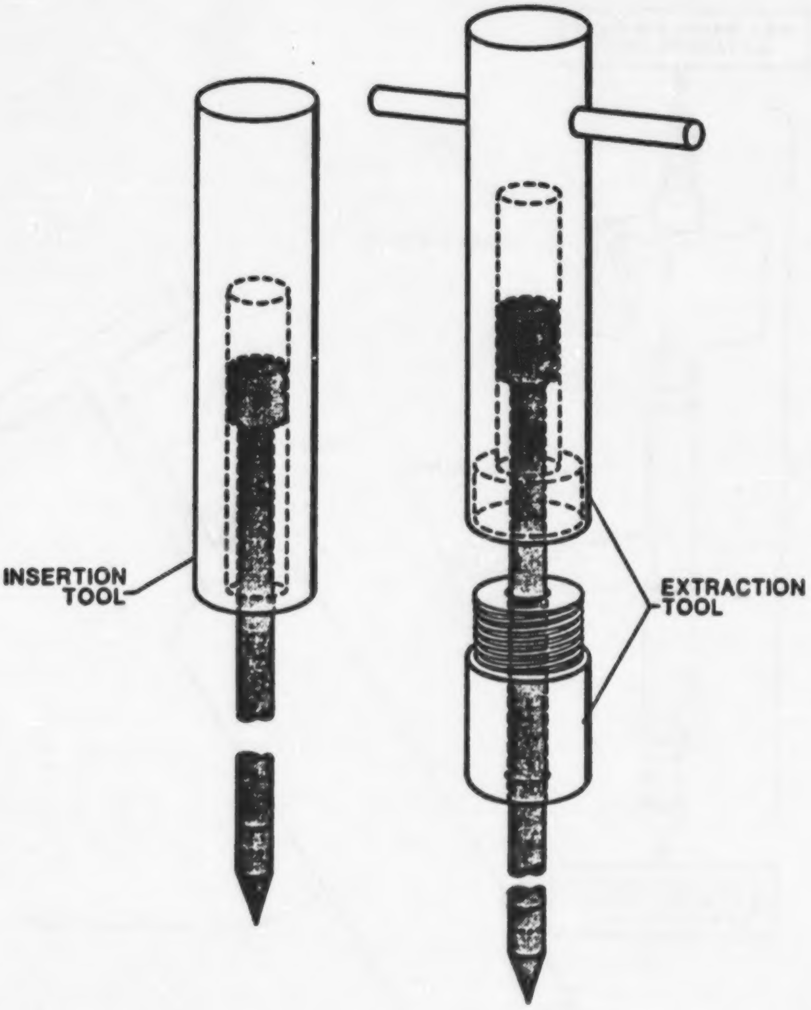

INSERTION TOOL
EXTRACTION TOOL

Figure 7.4. SOV probe driver and extractor.

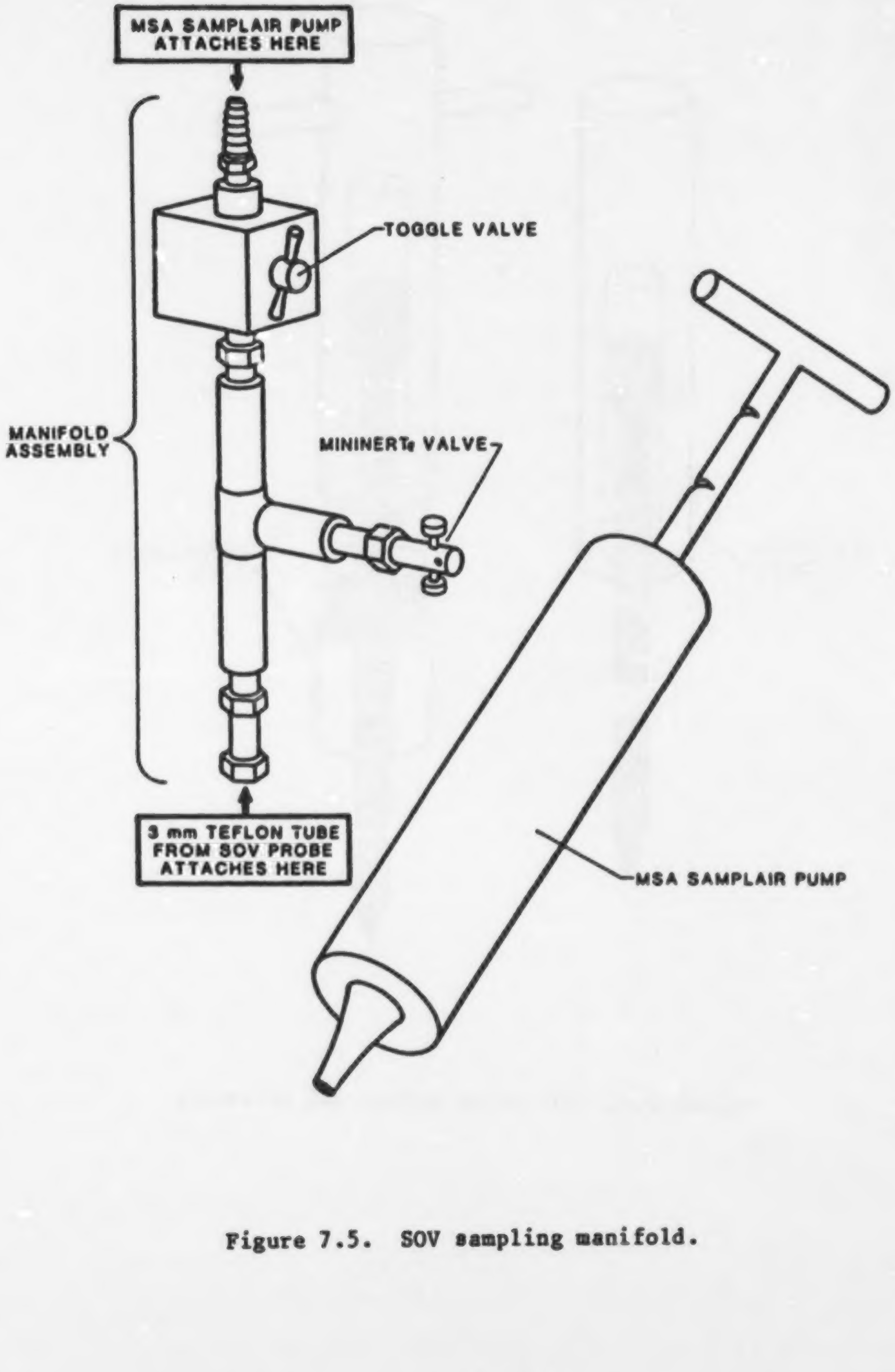

MSA SAMPLAIR PUMP ATTACHES HERE
TOGGLE VALVE
MANIFOLD ASSEMBLY
MININERT® VALVE
3 mm TEFLON TUBE FROM SOV PROBE ATTACHES HERE
MSA SAMPLAIR PUMP

Figure 7.5. SOV sampling manifold.

Analysis was performed with a Photovac Model 10A10 Portable Photoionization Gas Chromatograph designed to analyze volatile hydrocarbons including alkanes above ethane, and cyclic compounds such as benzene, toluene, xylene, and other aromatics. The detector of this particular GC was a vacuum ultraviolet photoionization system which ionizes hydrocarbons with bonding energies of 10.2 eV or less. Different hydrocarbons are detected with different efficiencies (different response per atom of carbon) in this device; the soil vapor data below are given in terms of the equivalent concentration of benzene.

Background concentrations of total non-methane hydrocarbons and five individual hydrocarbons in ambient air were measured at locations 2-km east and 2-km west of the study area; the observed values are listed in Table 7.1. Figure 7.6 shows the total non-methane hydrocarbon (NMHC) concentrations in soil gas as ppmv-benzene equivalents throughout the site. The hatched area outlines the location of the gasoline plume determined from drilling. From Table 7.1, background NMHC concentrations were on the order of 1.0 to 1.5 ppmv (benzene equivalent). Assuming that a NMHC soil-gas concentration of twice background defines the limits of the contaminant plume, the 3.0-ppmv NMHC soil-gas contour agrees reasonably well with the limits of the ground-water plume estimated from drilling. However, the NMHC soil-gas plume appears to lie north of the plume outline estimated from drilling, and soil gas concentrations in the vicinity of well SP6 are lower than those both upgradient and downgradient of well SP6.

Figures 7.7 through 7.11 show plots of the five organic vapor components measured: ethane/propane, butane, pentane, benzene, and isooctane. The lightest components, ethane/propane, do not correlate well with the gasoline plume. Ambient air background concentrations of these components were in the range of 0.6 to 1.4 ppmv (benzene equivalents), and the ethane/propane values shown on Figure 7.7 are in the range of 0.1 to 1.8 ppmv; these comparatively high background values may explain the behavior of these compounds. Pentane and benzene (Figures 7.9 and 7.10) were measured at concentrations above ambient air background values at only a few locations and were also poorly correlated with ground-water concentrations. Butane and isooctane (Figures 7.8 and 7.11, respectively) were measured in concentrations significantly above background, and yielded smooth contour plots which agreed well with the plume outlines estimated from ground-water sampling.

Vertical Cross-Sections

A vertical cross-section of relative organic vapor concentrations was established by drilling a north-south line

TABLE 7.1. BACKGROUND CONCENTRATIONS AS PPMV BENZENE

	2 km east of source	2 km west of source
Total NMHC	1.43	1.04
Ethane/Propane	1.43	.64
Butane	ND	.2
Pentane	ND	-
Hexane	ND	-
Heptane	ND	-
Iso-octane	ND	.2
Benzene	ND	ND
Other	ND	.2

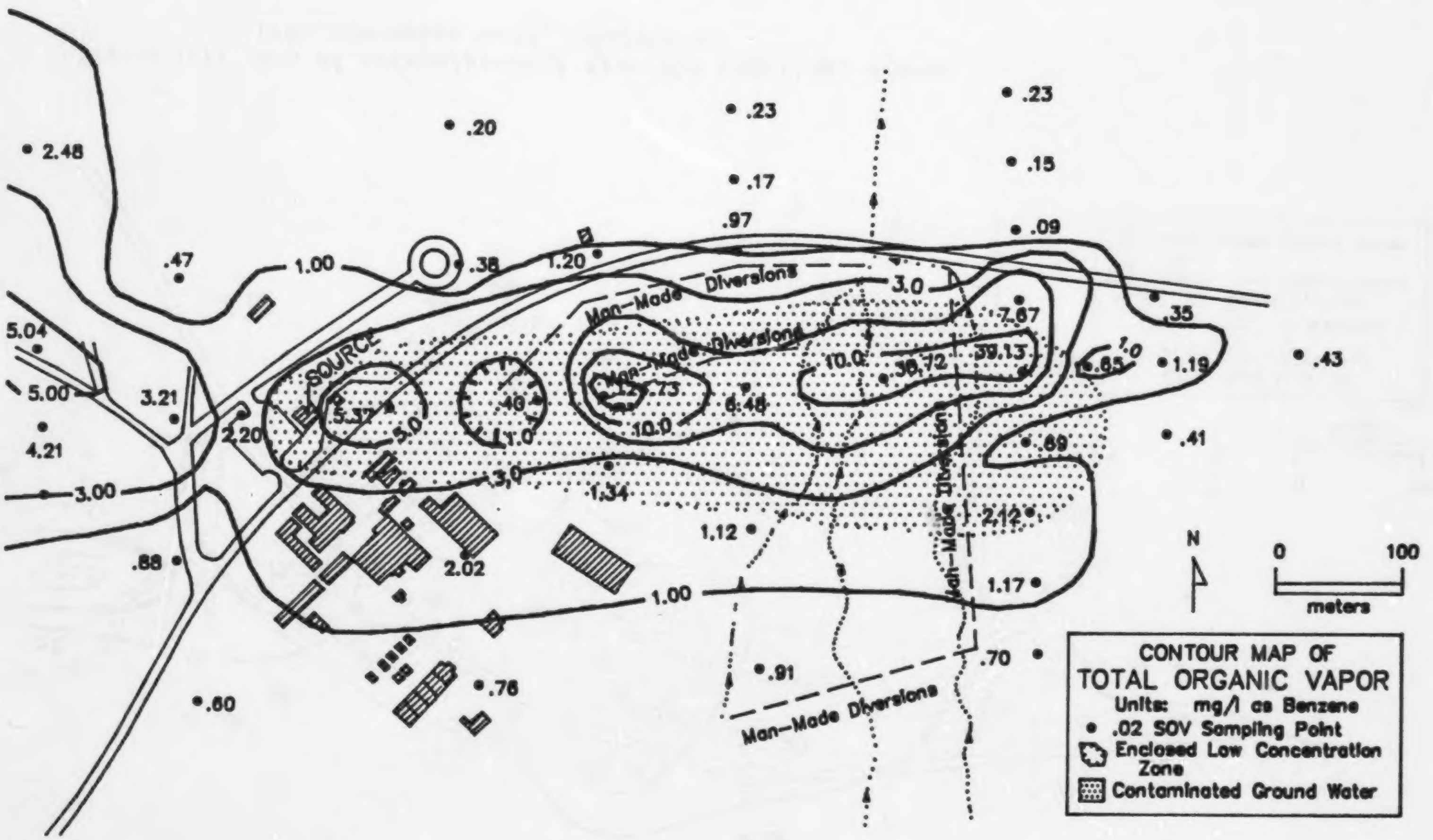

2.48
.20
.23
.23
.17
.15
.97
.09
.47
1.00
.38
1.20
Man-Made Diversions
3.0
5.04
SOURCE
7.87
5.00
3.21
5.37
5.0
.40
11.0
12.73
6.48
10.0
36.72
39.13
1.0
.85
.35
1.19
.43
4.21
2.20
10.0
.69
.41
3.00
3.0
1.34
2.12
1.12
.88
2.02
1.00
1.17
.70
.91
.78
.60
Man-Made Diversions
N
0
100
meters
CONTOUR MAP OF
TOTAL ORGANIC VAPOR
Units: mg/l as Benzene
• .02 SOV Sampling Point
Enclosed Low Concentration Zone
Contaminated Ground Water

Figure 7.6. Map of total organic vapor in ppm as benzene from SOV sampling, August 1984, Stovepipe Wells, California.

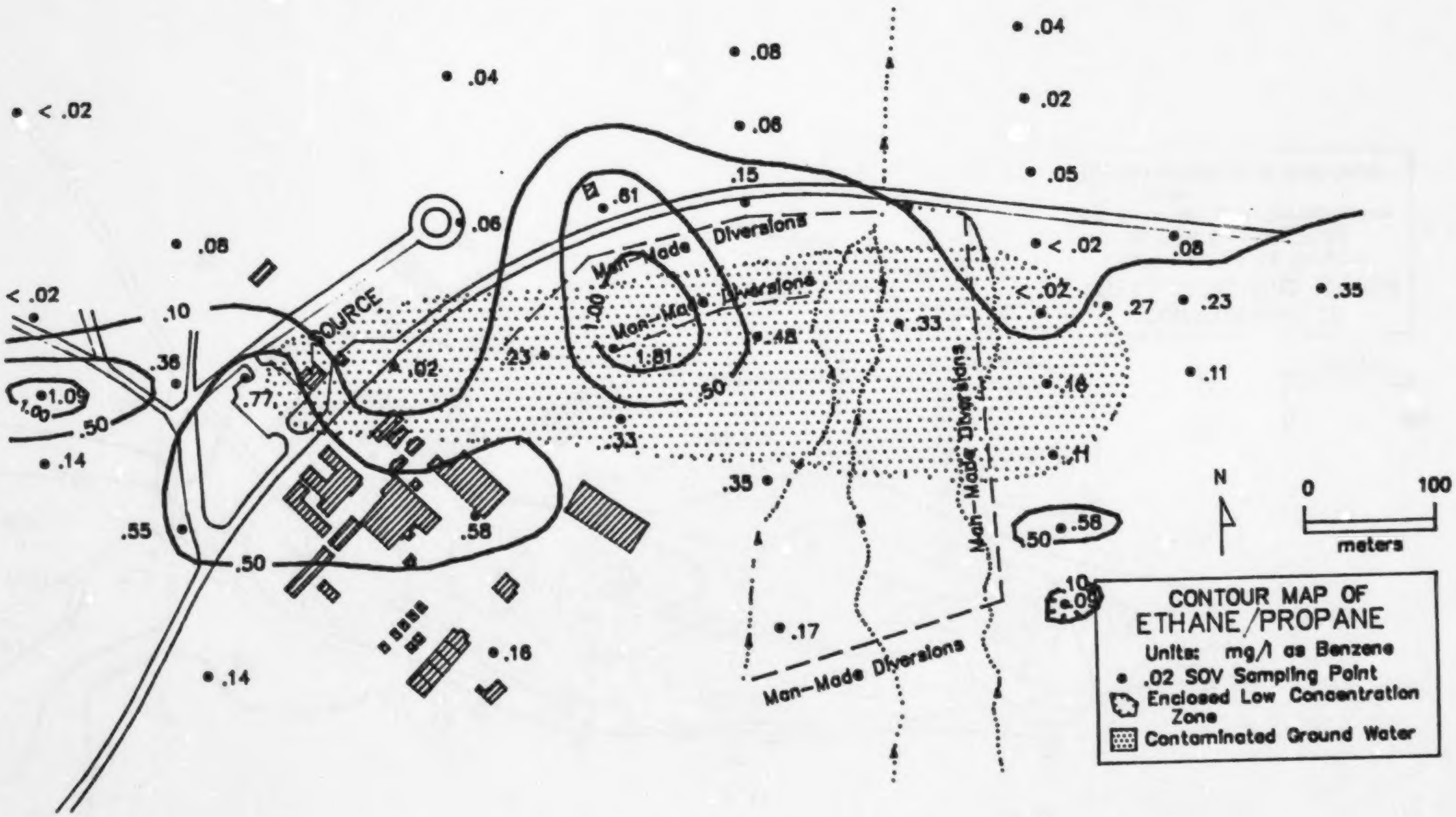

CONTOUR MAP OF
ETHANE/PROPANE
Units: mg/l as Benzene
• .02 SOV Sampling Point
Enclosed Low Concentration Zone
▨ Contaminated Ground Water
N
0
100
meters
SOURCE
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
< .02
.04
.08
.06
.08
.04
.02
.05
< .02
.08
.35
.27
.23
.11
< .02
.10
.36
1.09
1.00
.50
.14
.77
.55
.50
.02
.23
.81
1.00
1.81
.50
.48
.33
.15
.33
.16
.11
.35
.58
.58
.50
.10
.05
.17
.16
.14

Figure 7.7. Map of ethane/propane from SOV sampling, August 1984, Stovepipe Wells, California.

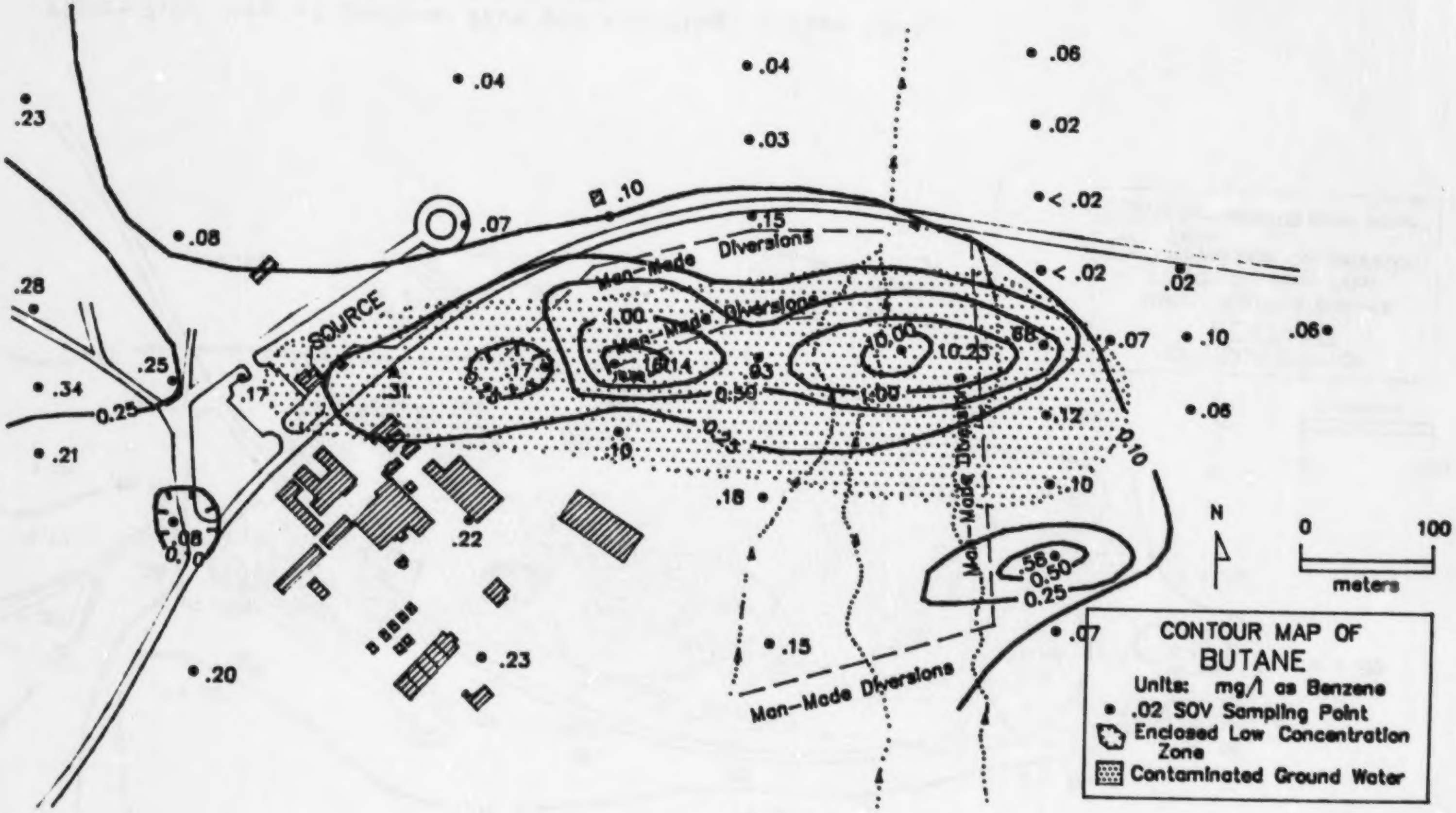

CONTOUR MAP OF
BUTANE
Units: mg/l as Benzene
.02 SOV Sampling Point
Enclosed Low Concentration Zone
Contaminated Ground Water
N
0
100
meters
SOURCE
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
1.00
1.00
0.50
0.25
0.10
10.00
10.25
1.00
16.14
.93
.68
.58
0.50
0.25
0.25
.23
.28
.34
.21
.25
.08
.17
.08
0.10
.20
.04
.07
.10
.31
.17
.22
.23
.10
.18
.15
.04
.03
.15
.06
.02
< .02
< .02
.02
.07
.10
.06
.12
.06
.10
.07

Figure 7.8. Map of butane from SOV sampling, August 1984, Stovepipe Wells, California.

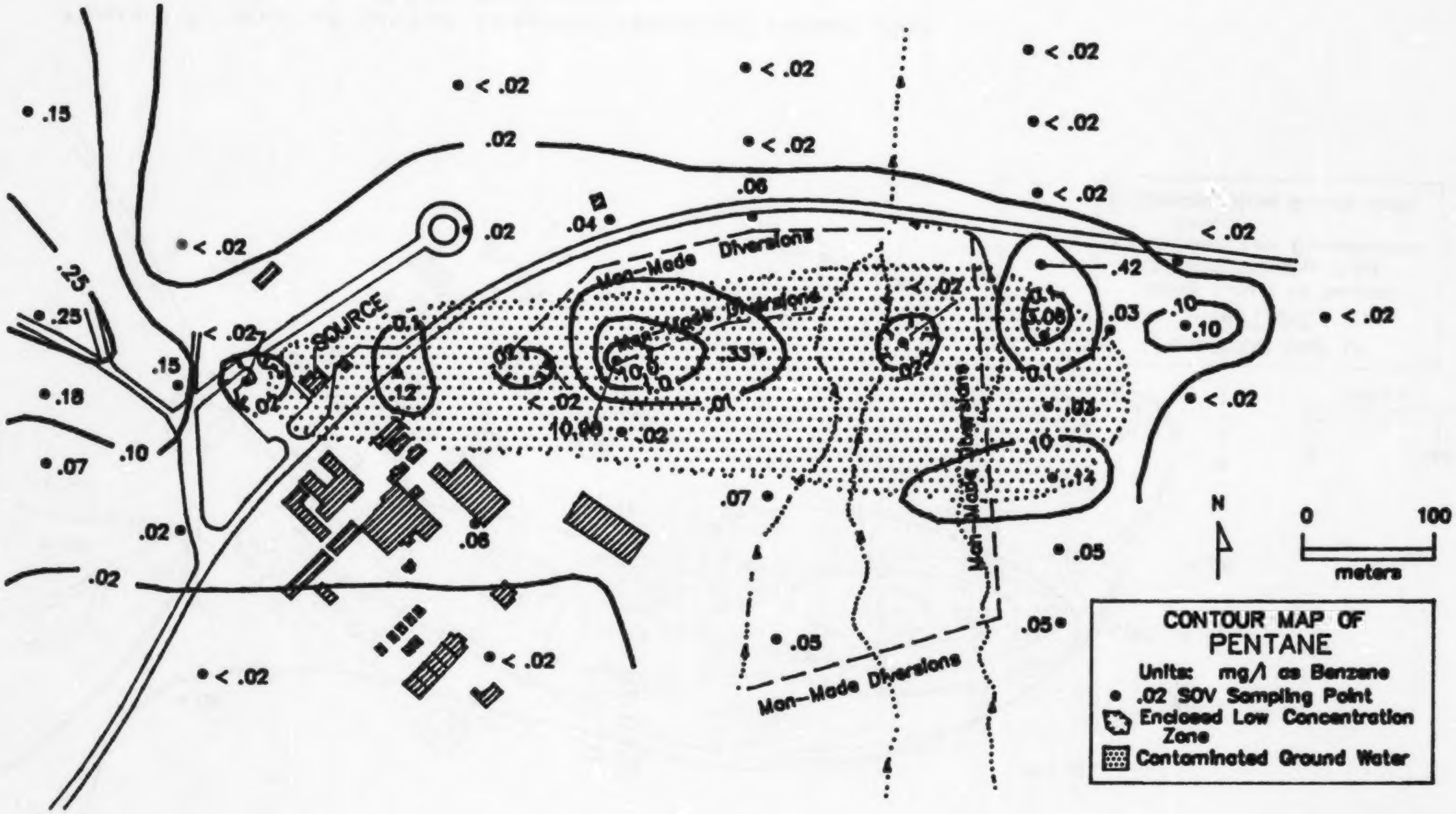

CONTOUR MAP OF
PENTANE
Units: mg/l as Benzene
● .02 SOV Sampling Point
Enclosed Low Concentration Zone
▨ Contaminated Ground Water
N
0
100
meters
SOURCE
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
.15
.25
.25
.18
.07
.10
.15
.02
.02
< .02
< .02
.02
.02
< .02
.04
.06
< .02
< .02
< .02
< .02
< .02
< .02
< .02
.42
.03
.10
.10
< .02
10.0
10.90
.02
.33
.01
< .02
.07
.05
.05
.05
.14
.10
.06
< .02
< .02
.12

Figure 7.9. Map of pentane from SOV sampling, August 1984, Stovepipe Wells, California.

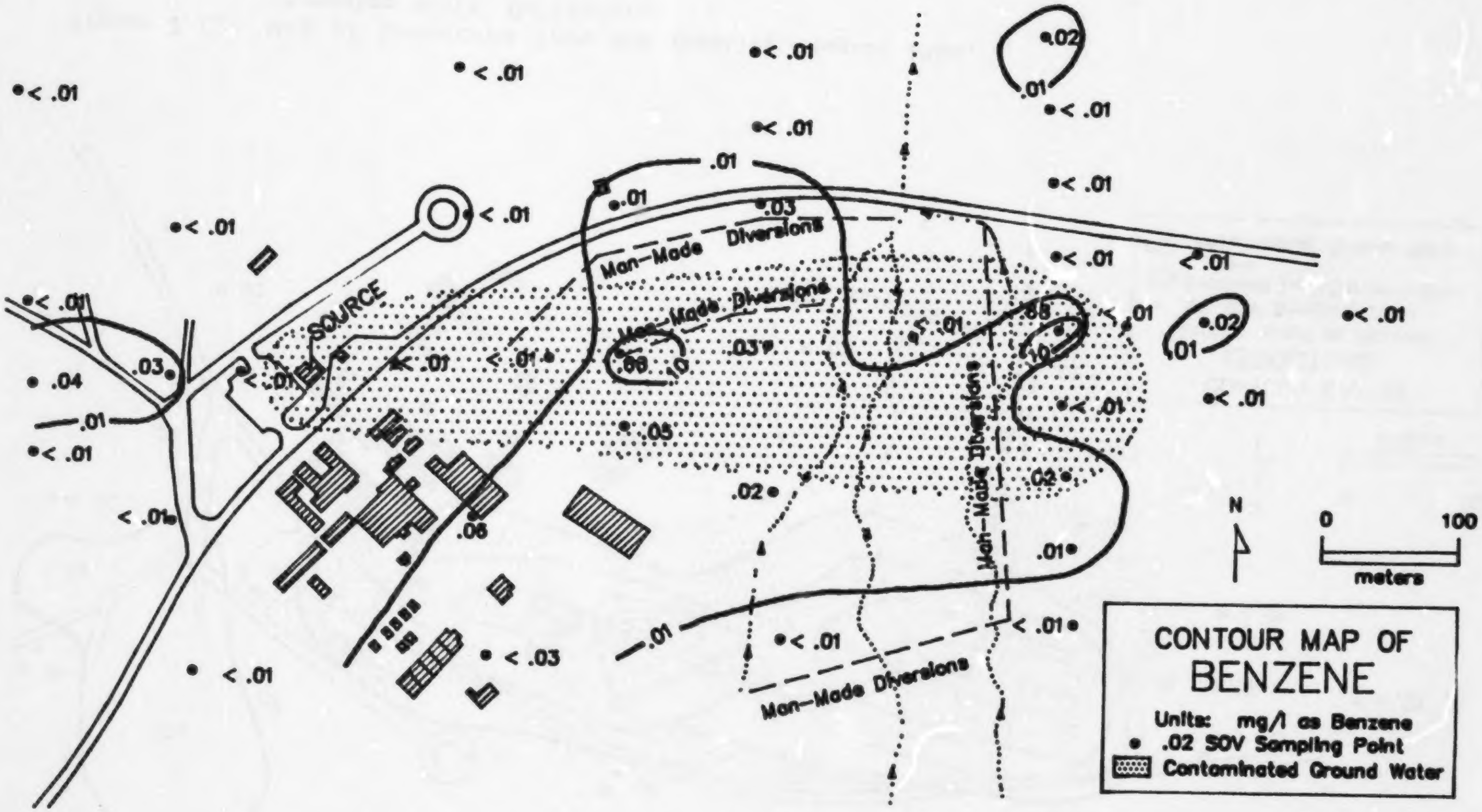

CONTOUR MAP OF
BENZENE
Units: mg/l as Benzene
● .02 SOV Sampling Point
▨ Contaminated Ground Water
N
0
100
meters
SOURCE
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
.01
.03
.04
.05
.06
.08
.10
.02
< .01
< .03

Figure 7.10. Map of Benzene from SOV sampling, August 1984, Stovepipe Wells, California.

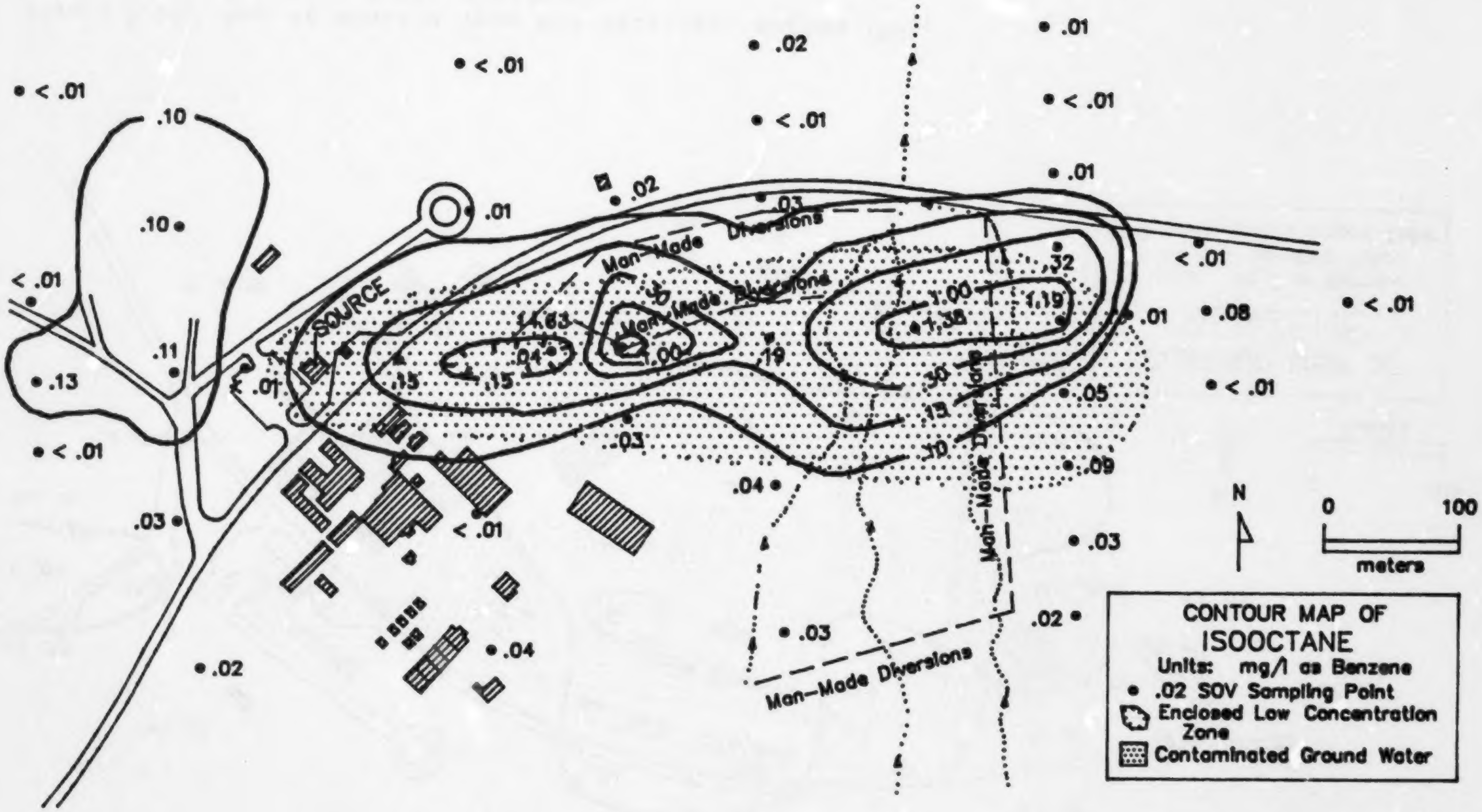

CONTOUR MAP OF
ISOOCTANE
Units: mg/l as Benzene
● .02 SOV Sampling Point
Enclosed Low Concentration Zone
▨ Contaminated Ground Water
N
0
100
meters
SOURCE
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
Man-Made Diversions
.10
.10
.11
.13
< .01
< .01
< .01
< .01
.03
.02
.01
.01
.02
< .01
.04
1.63
.15
.15
.04
.30
1.00
.03
.03
.02
< .01
.19
.04
.03
1.00
1.38
1.19
.32
.30
.13
.10
.01
< .01
.01
.05
.09
.03
.02
< .01
.01
.08
< .01
< .01

Figure 7.11. Map of isooctane from SOV sampling, August 1984, Stovepipe Wells, California.

of five wells across the ground-water plume. Four other wells were drilled for other purposes. Wells were drilled by using a hollow-stem auger to minimize disturbance of subsurface organic vapor concentrations. Samples were collected by driving a 2-inch ID split-spoon sampler, lined with four Shelby tubes each 4.5 inches long. Headspace analysis was used to evaluate the samples collected. This technique consisted of placing a soil sample in an airtight container, then sampling the headspace gases in the container after an equilibrium was reached between sample and headspace. The concentrations thus measured are relative; the values obtained are not the actual organic vapor concentrations in the soil but should be a linear function of the actual concentrations. Samples were transferred from the Shelby tubes directly into one-pint mason jars fitted with Mininert valves. Samples were allowed to stand for at least 3 hours at 24°C prior to analysis by gas chromatograph.

Figure 7.12 is a qualitative summary of well-drilling results across the Stovepipe Wells study site. Figure 7.13 shows vertical profiles of ethane/propane, butane, benzene, pentane, and isooctane observed in headspace samples from well SP5 which is considered to be a background well. Concentrations of these components remain relatively constant at all depths both above and below the water table. Figures 7.14 through 7.18 show vertical cross-sections of headspace concentrations of ethane/propane, butane, benzene, pentane, and isooctane observed in samples from wells 36J1, SP4, SP1, SP3, and SP2. This five-well transect lies perpendicular to the axis of the plume near its leading edge; at this location no free product was observed standing on the water table while only gasoline components dissolved in ground-water were observed. Along the cross-section, contamination appears to extend downward into the water table for several feet. In the vadose zone, ethane/propane and butane occur in greatest concentration just above the water table, as expected.

Conclusions

The survey of organic vapors in soils confirmed the position of the contaminant plume delineated by ground-water sampling. Butane, isooctane, and total organic vapors were correlated strongly with ground-water concentrations; plume limits determined from these soil-gas components agreed well with well-sampling results both in plume location and extent. Ethane/propane had weaker correlations probably because their ambient air background concentrations were of the same order of magnitude as the soil-gas concentrations.

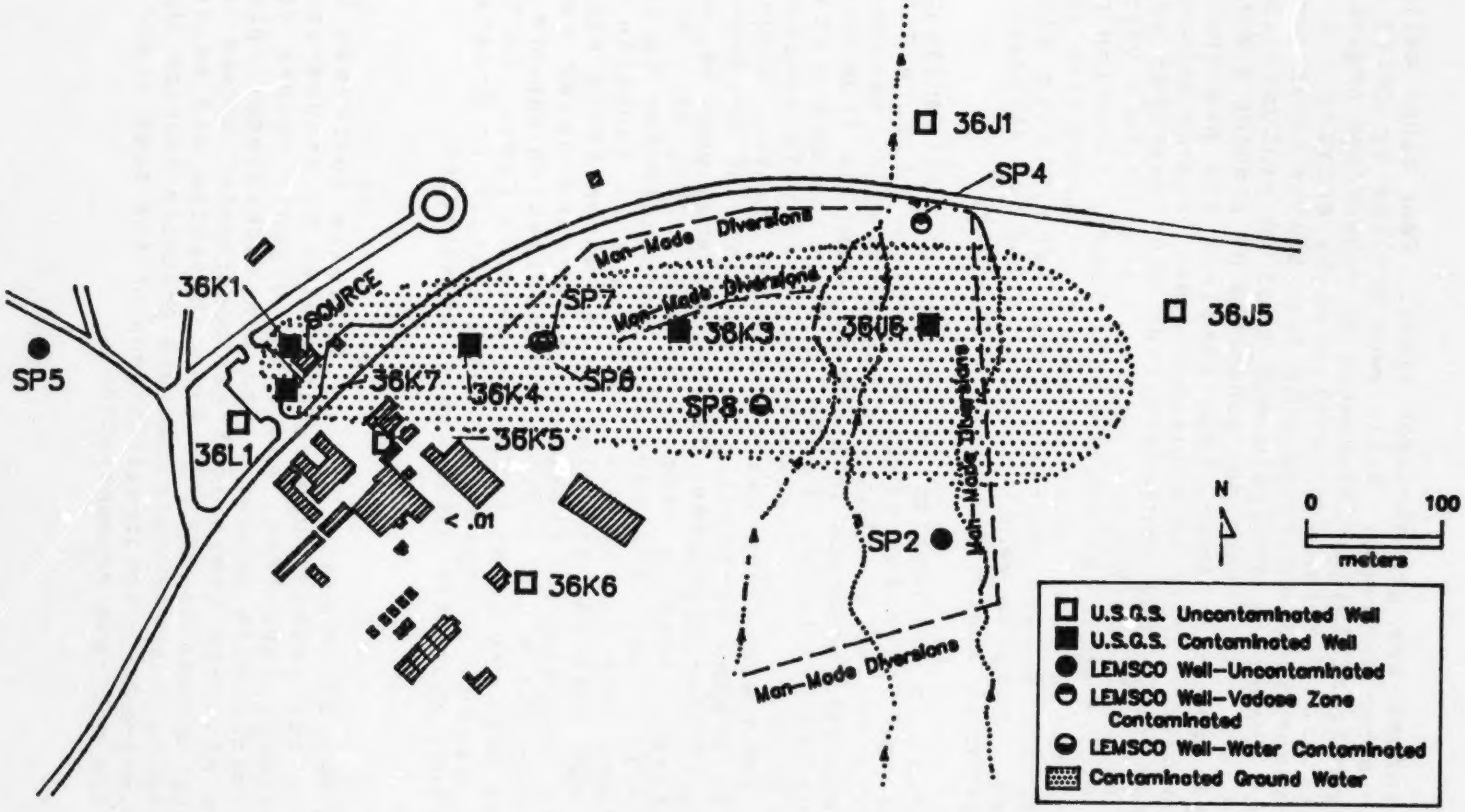

36J1
SP4
36J5
SOURCE
36K1
SP5
36K7
36K4
SP7
SP6
Man-Made Diversions
Man-Made Diversions
36K3
36J6
SP8
36K5
36L1
< .01
36K6
SP2
Man-Made Diversions
Man-Made Diversions
N
0
100
meters
□ U.S.G.S. Uncontaminated Well
■ U.S.G.S. Contaminated Well
● LEMSCO Well-Uncontaminated
◒ LEMSCO Well-Vadose Zone Contaminated
◓ LEMSCO Well-Water Contaminated
▨ Contaminated Ground Water

Figure 7.12. Summary of drilling results, August 1984, Stovepipe Wells, California.

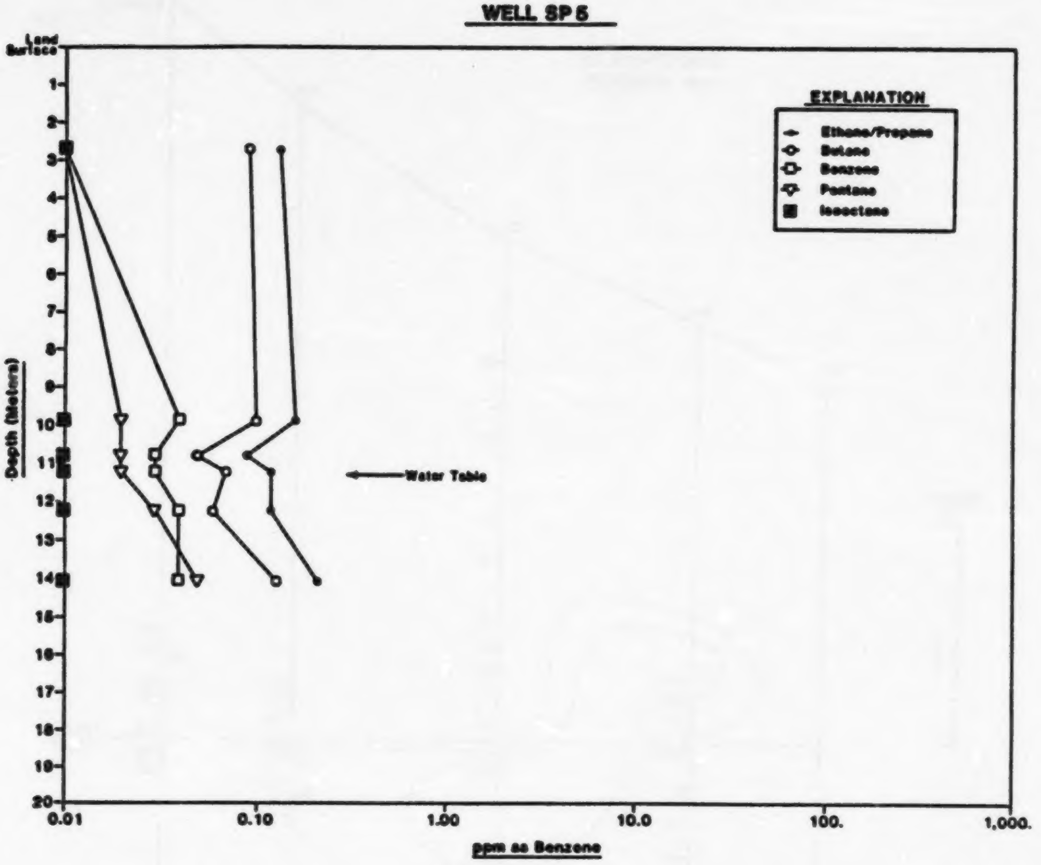
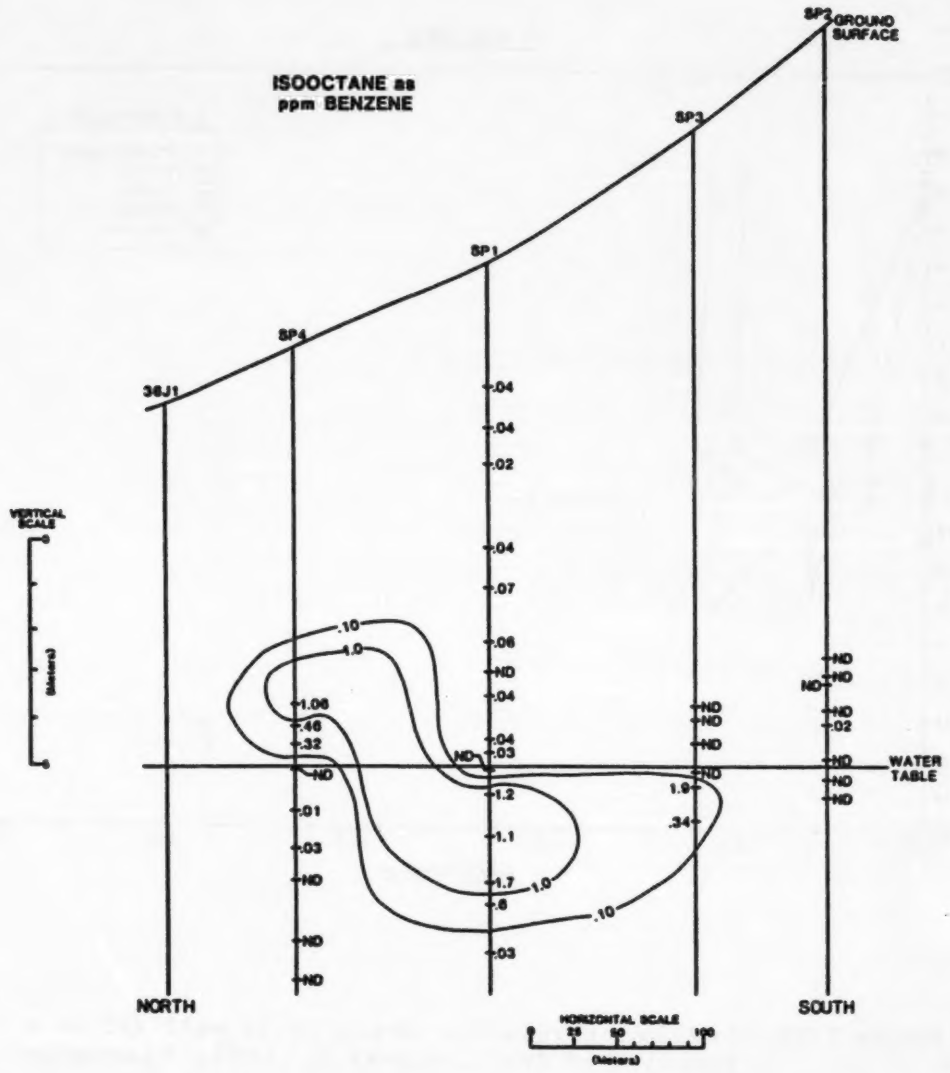
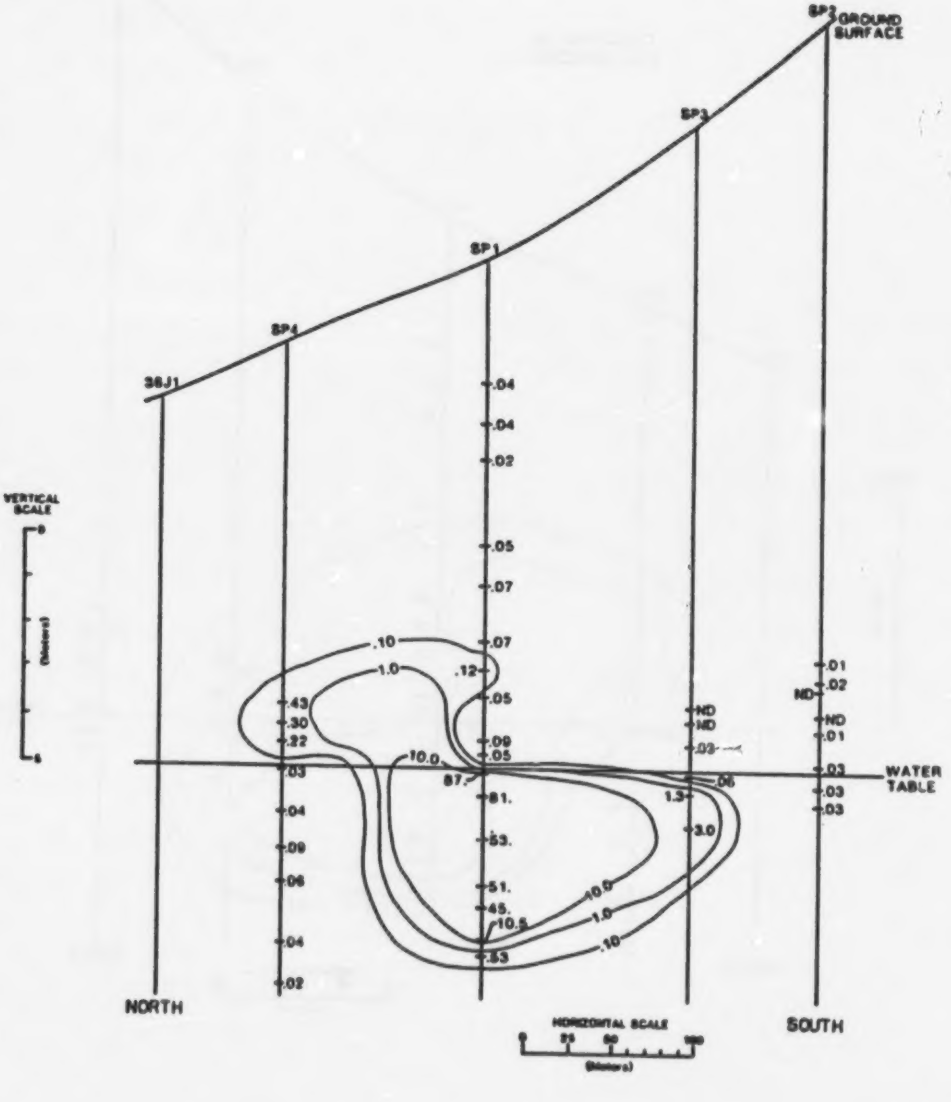


Figure 7.13. Levels of volatile organics in well SP5 as a function of depth, August 5, 1984, Stovepipe Wells, California.



ISOOCTANE as
ppm BENZENE
SP2
GROUND SURFACE
SP3
SP1
SP4
36J1
VERTICAL SCALE
(Meters)
.04
.04
.02
.04
.07
.06
ND
.04
.04
.03
ND
1.2
1.1
1.7
.6
.03
.10
1.0
1.06
.46
.32
ND
.01
.03
ND
ND
ND
ND
ND
ND
ND
1.9
.34
ND
ND
ND
ND
.02
ND
ND
ND
WATER TABLE
NORTH
SOUTH
HORIZONTAL SCALE
0
25
50
100
(Meters)

Figure 7.14. Cross-section of isooctane levels (ppm) across the contaminant plume, August 1984, Stovepipe Wells, California.



SP2
GROUND SURFACE
SP3
SP1
SP4
36J1
VERTICAL SCALE
(Meters)
.04
.04
.02
.05
.07
.07
.10
1.0
.12
.05
.43
.30
.22
.09
.05
10.0
.03
87.
81.
.04
53.
.09
.06
51.
45.
10.5
10.0
1.0
.10
.04
.53
.02
ND
ND
.03
.06
1.3
3.0
.01
.02
ND
ND
.01
.03
.03
.03
WATER TABLE
NORTH
SOUTH
HORIZONTAL SCALE
0
25
50
100
(Meters)

Figure 7.15. Cross-section of benzene levels (ppm) across the contaminant plume, August 1984, Stovepipe Wells, California.

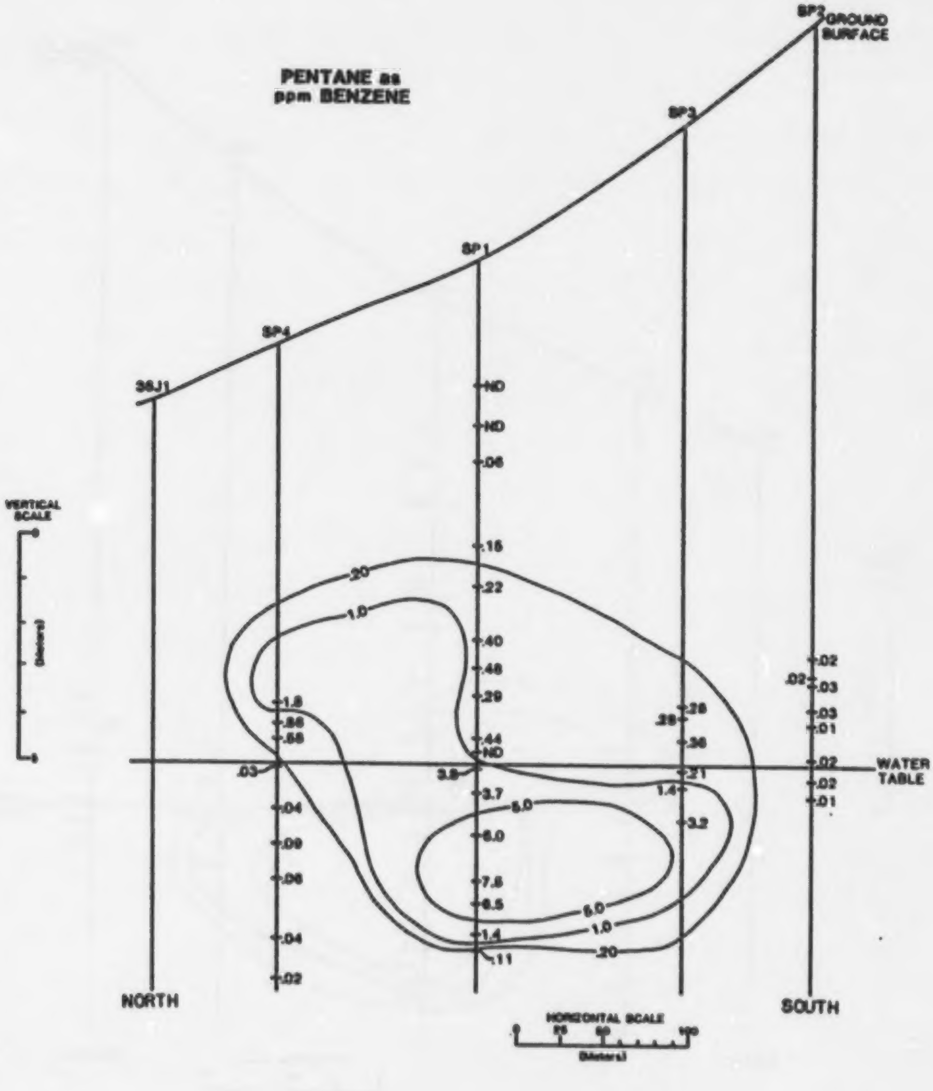

PENTANE as ppm BENZENE
SP2
GROUND SURFACE
SP3
SP1
SP4
36J1
VERTICAL SCALE
(Meters)
ND
ND
.06
.16
.22
.40
.48
.29
.44
ND
3.8
3.7
6.0
7.6
6.5
1.4
.11
1.8
.86
.68
.03
.04
.09
.06
.04
.02
.26
.28
.36
.21
1.4
3.2
.02
.02
.03
.03
.01
.02
.02
.01
.20
1.0
5.0
5.0
1.0
.20
WATER TABLE
NORTH
SOUTH
HORIZONTAL SCALE
0
25
50
100
(Meters)

Figure 7.16. Cross-section of pentane levels (ppm) across the contaminant plume, August 1984, Stovepipe Wells, California.

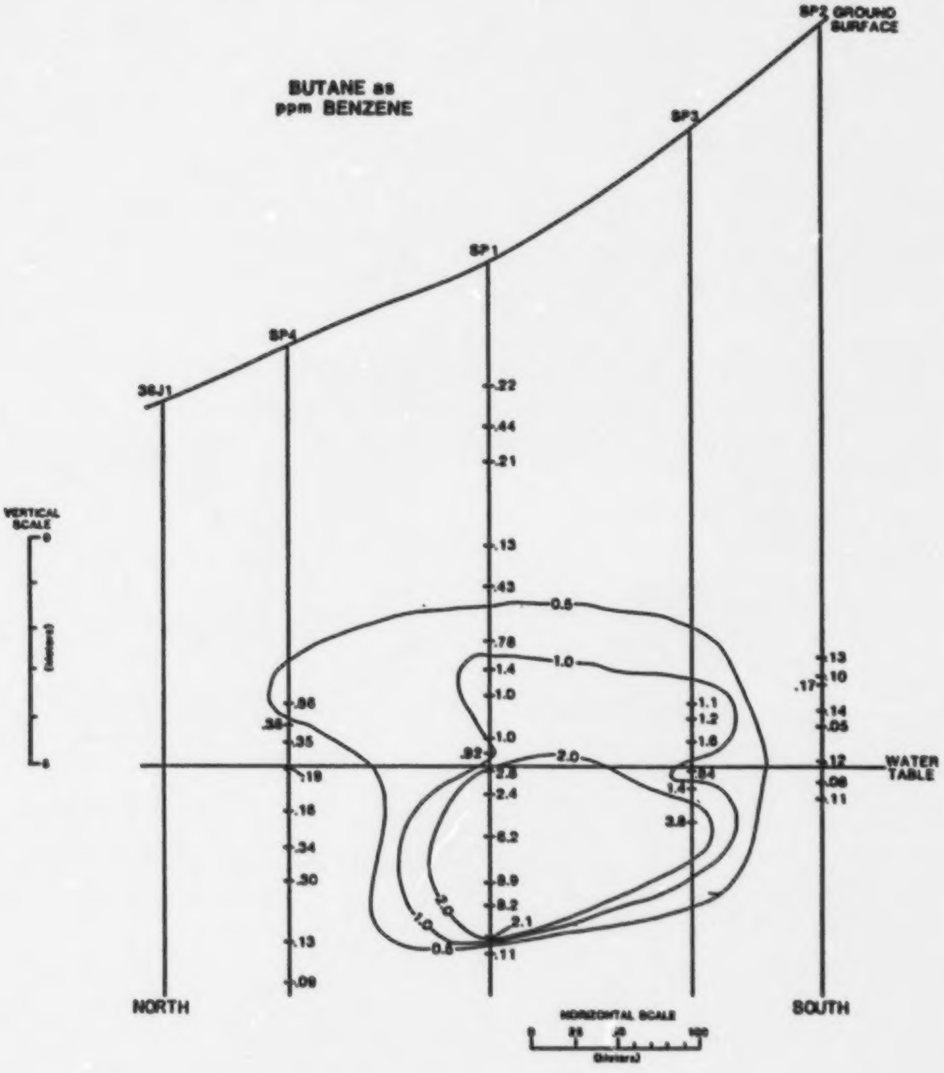

BUTANE as
ppm BENZENE
SP2 GROUND SURFACE
SP3
SP1
SP4
36J1
VERTICAL SCALE
0
5
(Meters)
.22
.44
.21
.13
.43
0.5
.78
1.0
1.4
1.0
1.0
.92
2.0
2.8
2.4
6.2
8.9
8.2
2.1
.11
2.0
1.0
0.5
.86
.36
.35
.19
.16
.34
.30
.13
.09
1.1
1.2
1.6
.84
1.4
3.8
13
.17
10
14
.05
12
.06
.11
WATER TABLE
NORTH
SOUTH
HORIZONTAL SCALE
0
25
50
100
(Meters)

Figure 7.17. Cross-section of butane levels (ppm) across the contaminant plume, August 1984, Stovepipe Wells, California.

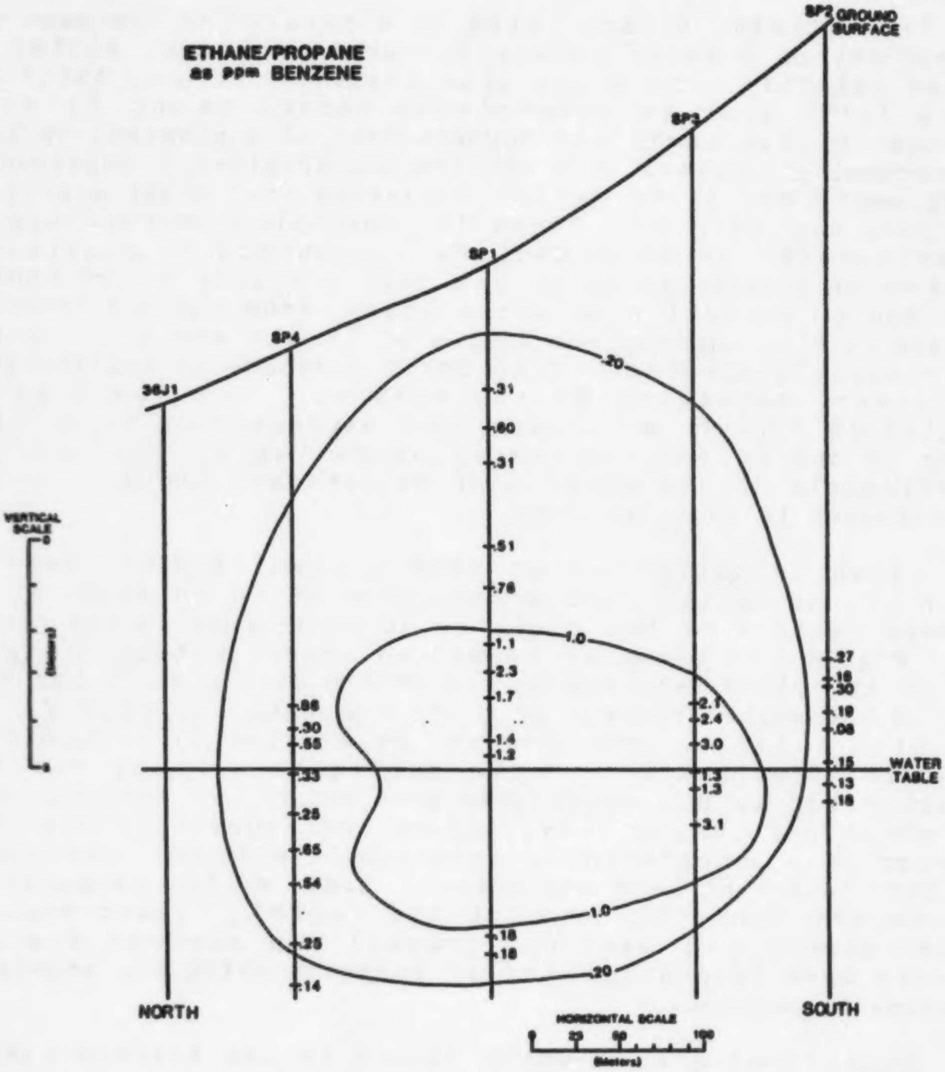

ETHANE/PROPANE
as ppm BENZENE
SP2 GROUND SURFACE
SP3
SP1
SP4
36J1
VERTICAL SCALE
0
5
(Meters)
.20
1.0
.31
.60
.31
.51
.76
1.1
2.3
1.7
1.4
1.2
.18
.18
.86
.30
.55
.33
.25
.65
.54
.25
.14
2.1
2.4
3.0
1.3
1.3
3.1
.27
.18
.30
.19
.08
.15
.13
.18
WATER TABLE
NORTH
SOUTH
HORIZONTAL SCALE
0
25
50
100
(Meters)

Figure 7.18. Cross-section of ethane/propane levels (ppm) across the contaminant plume, August 1984, Stovepipe Wells, California.

STUDY OF GROUND-WATER CONTAMINATION FROM INDUSTRIAL SOURCES AT PITTMAN, NEVADA

The Pittman, Nevada, site is a portion of the east-west right-of-way of a major municipal supply aqueduct called the Pittman Lateral. The study site (Walther, et al., 1983) (see Figure 7.19) lies in undeveloped desert about 11 miles southeast of Las Vegas and downgradient of a chemical refining and processing complex. The complex was originally constructed during World War II to refine manganese ore; other activities which have been performed there include titanium refining and the production of intermediate components of pesticides. Ground-water contamination at the site probably began shortly after the construction of the complex; from the mid-1940's to the late 1970's, unknown quantities of liquid and solid wastes were routinely disposed of in leach pits and in unlined ponds on property belonging to the complex. A major leak was detected in 1976 in an underground storage tank on property leased by one of the companies operating in the complex. Approximately 30,000 gallons of benzene are thought to have been released in that incident.

Depth to ground-water varies significantly over the length of the contaminant plume, from 55 to 60 feet at the southern regions of the plume to 10 to 12 feet in the Pittman area. Figure 7.20 shows an idealized cross-section along the axis of the plume from the source to its discharge in Las Vegas Wash. A hydraulic gradient of 0.012 has been reported for the area with a linear ground-water flow velocity estimated in excess of 1000 feet/year. The surficial geology has been characterized as unconsolidated sand and gravel alluvium 30 to 100 feet thick. Below these layers the hydrologic bottom is composed of a comparatively impermeable mudstone interspersed with thin layers of sand and gravel. Bands of low permeability caliche are found throughout the region. Paleo-channels (buried deposits of sand and gravel) and surface drainage channels have been suggested as conduits which may accelerate contaminant movement.

Unconfined ground-water occurs in the Pittman Lateral area at depths of 6 to 12 feet in calcified but unconsolidated alluvium. Since the early 1970's, a series of monitoring wells have been installed by the company responsible for the benzene leak and by the U.S. Bureau of Reclamation. Figure 7.21 shows concentrations of total dissolved solids in ground-water measured in monitoring wells in the area downgradient of the industrial complex. From hydrologic studies by the company responsible for the benzene spill, a plume of organic solvents and pesticides was identified; Figure 7.22 shows isoconcentration lines of benzene in ground-water. The areal extent of the solvent plume is about 0.6 square miles and underlies residential and commercial portions of Pittman.

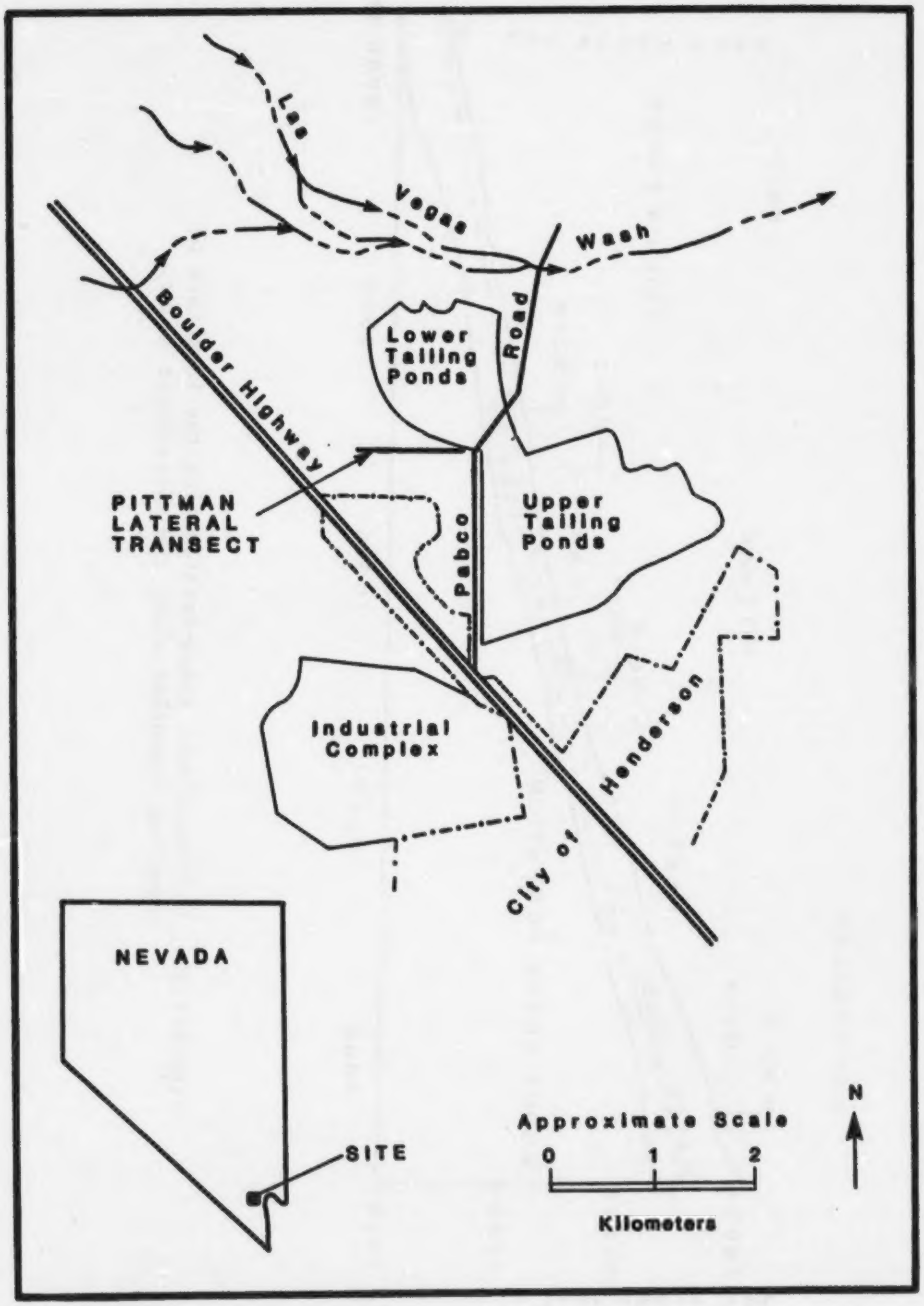

Las
Vegas
Wash
Boulder Highway
Road
Lower
Tailing
Ponds
Upper
Tailing
Ponds
Pabco
PITTMAN
LATERAL
TRANSECT
Industrial
Complex
City of Henderson
NEVADA
SITE
Approximate Scale
0
1
2
Kilometers
N

Figure 7.19. General location map.

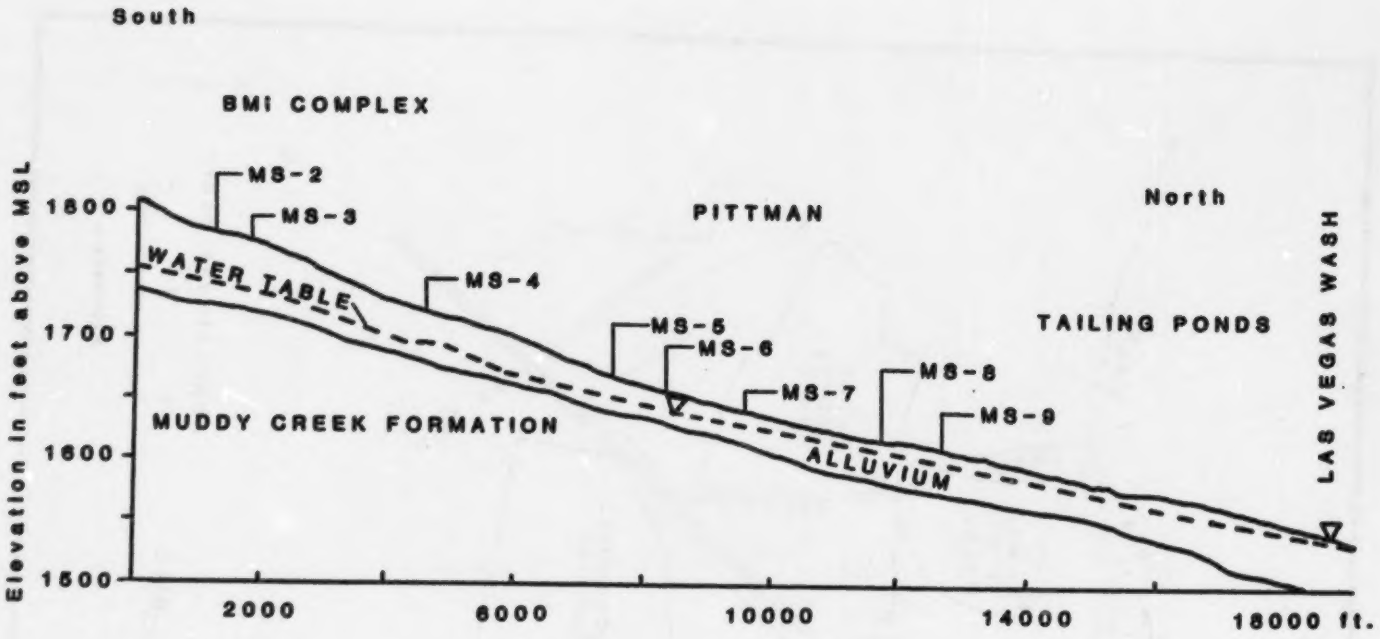

South
BMI COMPLEX
MS-2
MS-3
MS-4
MS-5
MS-6
MS-7
MS-8
MS-9
PITTMAN
North
TAILING PONDS
LAS VEGAS WASH
WATER TABLE
ALLUVIUM
MUDDY CREEK FORMATION
Elevation in feet above MSL
1800
1700
1600
1500
2000
6000
10000
14000
18000 ft.

Figure 7.20. Hydrogeologic cross-section with the locations of sampling boreholes along the contaminant plume.

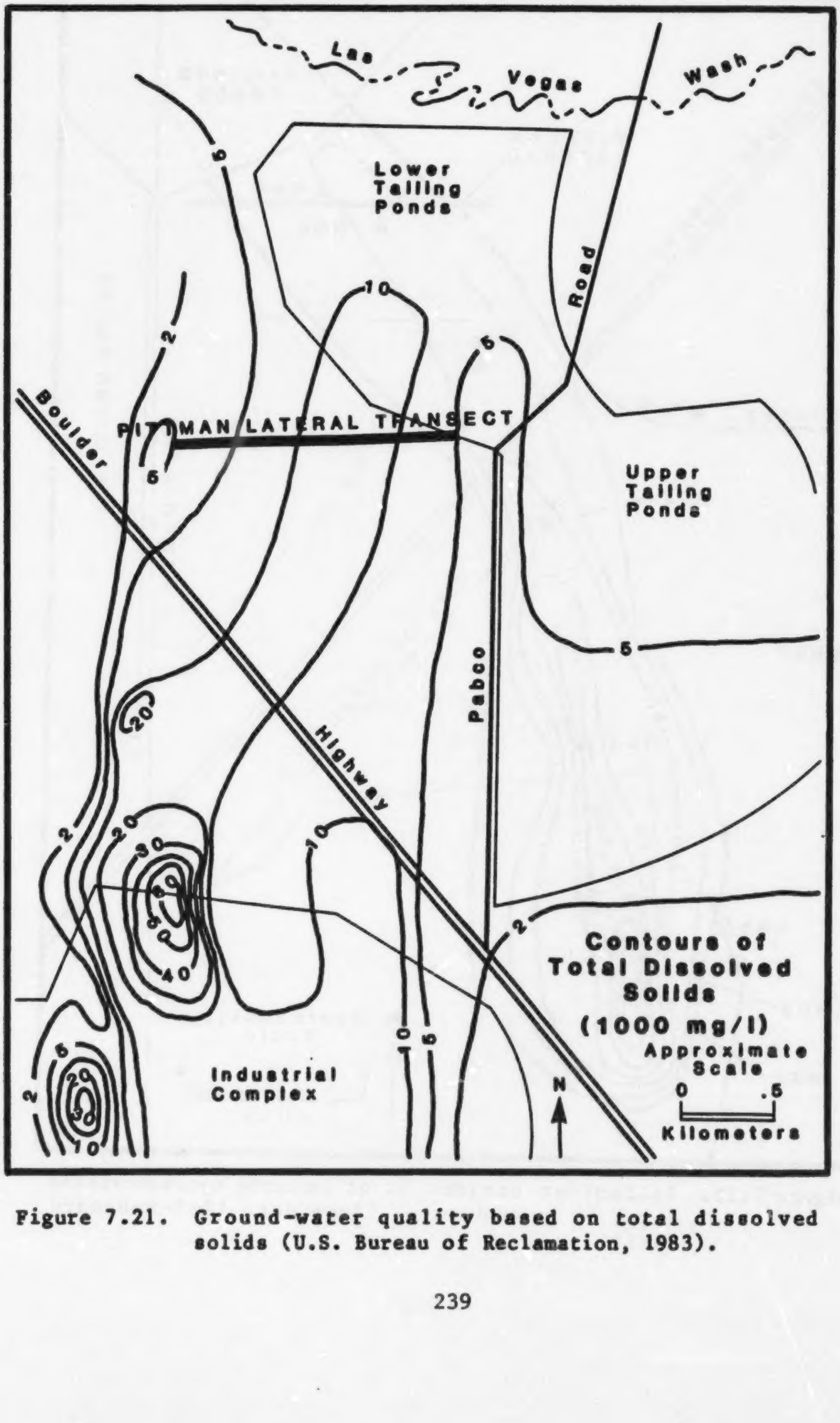

Las Vegas Wash
Lower Tailing Ponds
Road
Upper Tailing Ponds
PITTMAN LATERAL TRANSECT
Boulder Highway
Pabco
Industrial Complex
Contours of Total Dissolved Solids (1000 mg/l)
Approximate Scale
0 .5
Kilometers
N
2
5
10
20
30
40
5
10
2

Figure 7.21. Ground-water quality based on total dissolved solids (U.S. Bureau of Reclamation, 1983).

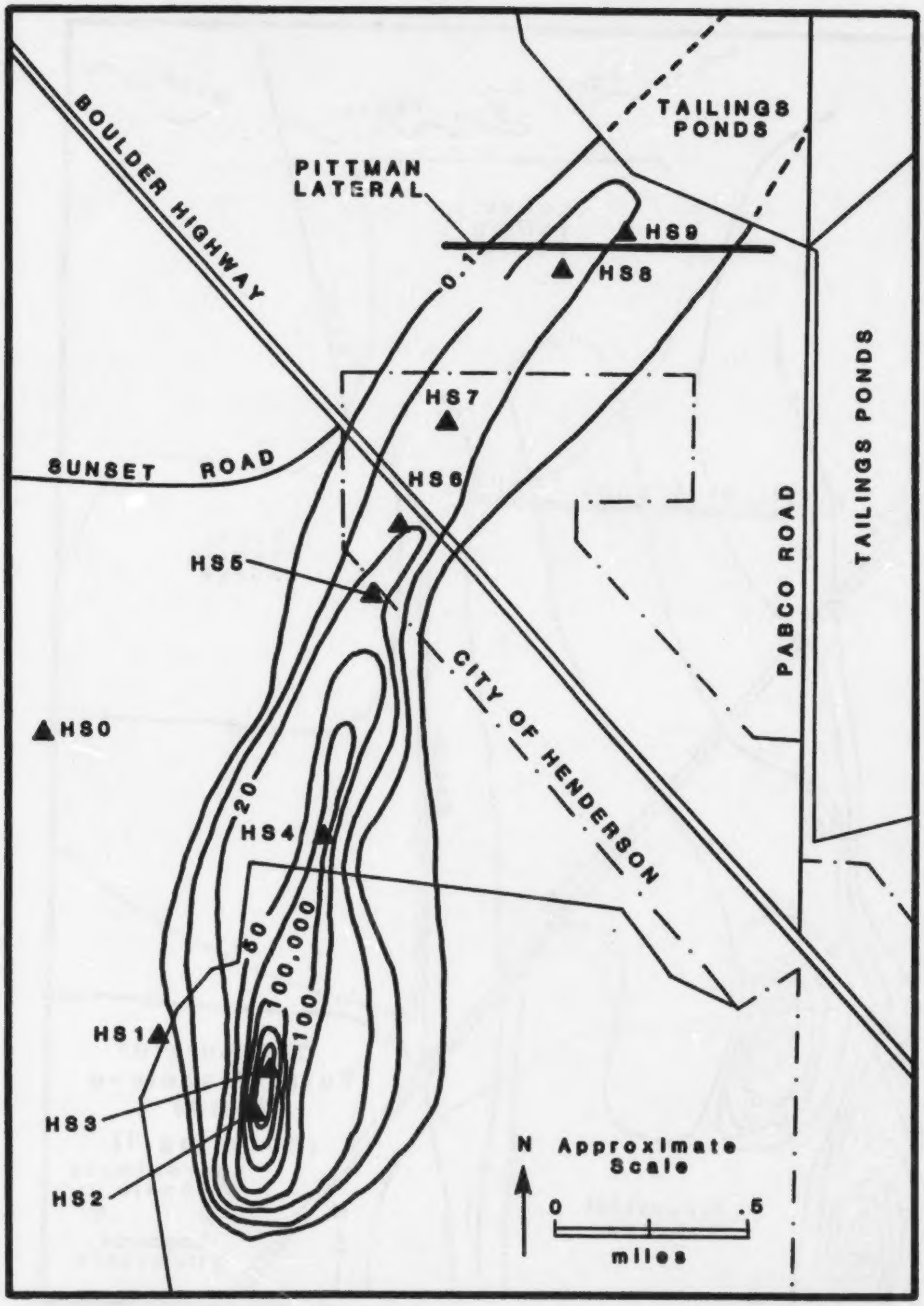

TAILINGS PONDS
PITTMAN LATERAL
BOULDER HIGHWAY
HS9
HS8
0.1
HS7
SUNSET ROAD
HS6
HS5
CITY OF HENDERSON
PABCO ROAD
TAILINGS PONDS
HS0
20
HS4
50
100,000
100
HS1
HS3
HS2
N
Approximate Scale
0
.5
miles

Figure 7.22. Isocontour projection of benzene concentrations (ppm) in ground-water (from data 1982-February 1983).

Benzene concentrations in ground-water have been reported to range from in excess of 500,000 mg/l near the source to 5-10 mg/l in the vicinity of the Pittman lateral. These contaminant plumes move downgradient through the unconfined aquifer from the industrial complex through the study area to discharge ultimately in Las Vegas Wash, the major surface and subsurface drainage path for the Las Vegas Valley. Figure 7.23 is a cross-section along the Pittman Lateral (perpendicular to the plume) of the vadose zone, the unconfined aquifer, and the underlying clay formation which forms a barrier to downward movement from the unconfined aquifer. Figure 7.24 shows the study area and the locations of monitoring wells, the drilling logs for these locations provided the information used to prepare Figure 7.23. The ground-water contains a variety of organic and inorganic contaminants. However, the volatile organic compounds of interest to this study are chloroform in the contaminant plume on the eastern side of the site and benzene and chlorobenzene in the plume on the western side. Tables 7.2 and 7.3 list the monitoring wells which were sampled together with their respective concentrations of chloroform, benzene, and chlorobenzene, as well as the dates of sampling. Figure 7.25 is a plot of the ground-water concentrations of these three compounds as a function of distance along the Pittman Lateral, perpendicular to the plume. Figure 7.25 shows that there are two distinct plumes: one plume on the eastern end of the study area exhibiting significant concentrations of chloroform, and another to the west exhibiting large concentrations of benzene and chlorobenzene.

As a test of the soil-gas sampling system described in the Stovepipe Wells case study (Figures 7.3-7.5), soil-gas sampling was conducted along the Pittman Lateral to develop profiles of volatile organic concentrations (Kerfoot and Barrows, 1985). Figures 7.26 and 7.27 show the sampling plan for a series of samples collected at a 4-foot depth. Figure 7.26 shows the sampling plan used over the chloroform plume while Figure 7.27 shows the sampling plan used over the benzene/chlorobenzene plume.

For chloroform analysis, the AID gas chromatograph with electron-capture detector (AID GC/ECD) was selected; this instrument has relatively high sensitivity to chloroform. The chromatograph column was a stainless steel tube, 1/8-inch in ID and 6 feet in length packed with 10 percent DC-200 on 80/100-mesh Chromosorb HP. The detector and injection port operated at 37°C; the column, at 43°C. The carrier gas was approximately 20 cm^3/min of 5 percent methane in argon (P-5). The chloroform detection limit for the AID GC/ECD was 5 ppbv. Sample sets from each probe location and depth point consisted of two or three Hamilton Series 100 Gastight syringes. These were 250 ul capacity except for the vertical profile study

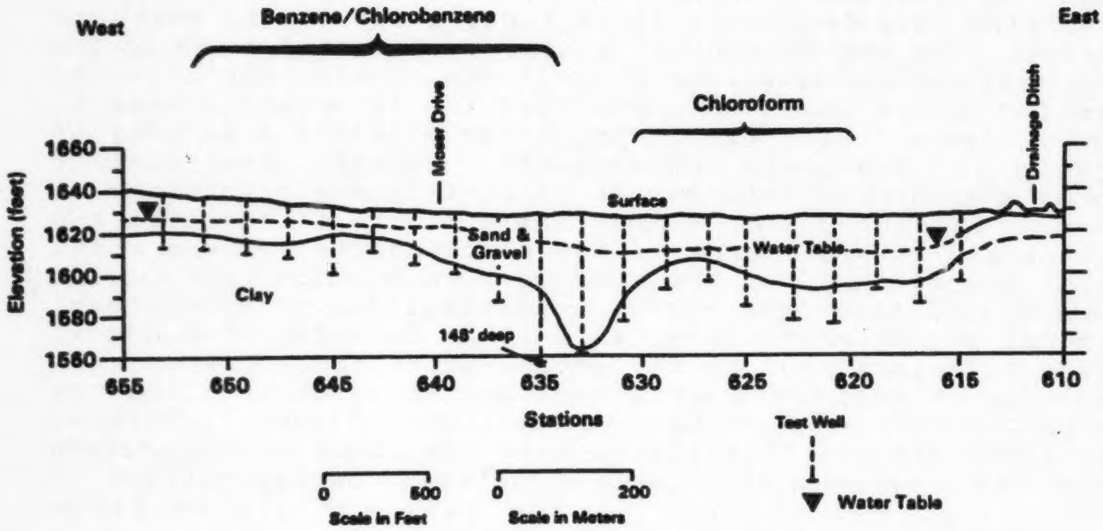

West
Benzene/Chlorobenzene
East
Moser Drive
Chloroform
Drainage Ditch
Elevation (feet)
1660
1640
1620
1600
1580
1560
Surface
Sand & Gravel
Water Table
Clay
148' deep
655
650
645
640
635
630
625
620
615
610
Stations
Test Well
Water Table
0
500
Scale in Feet
0
200
Scale in Meters

Figure 7.23. Hydrogeologic cross section of the transect.

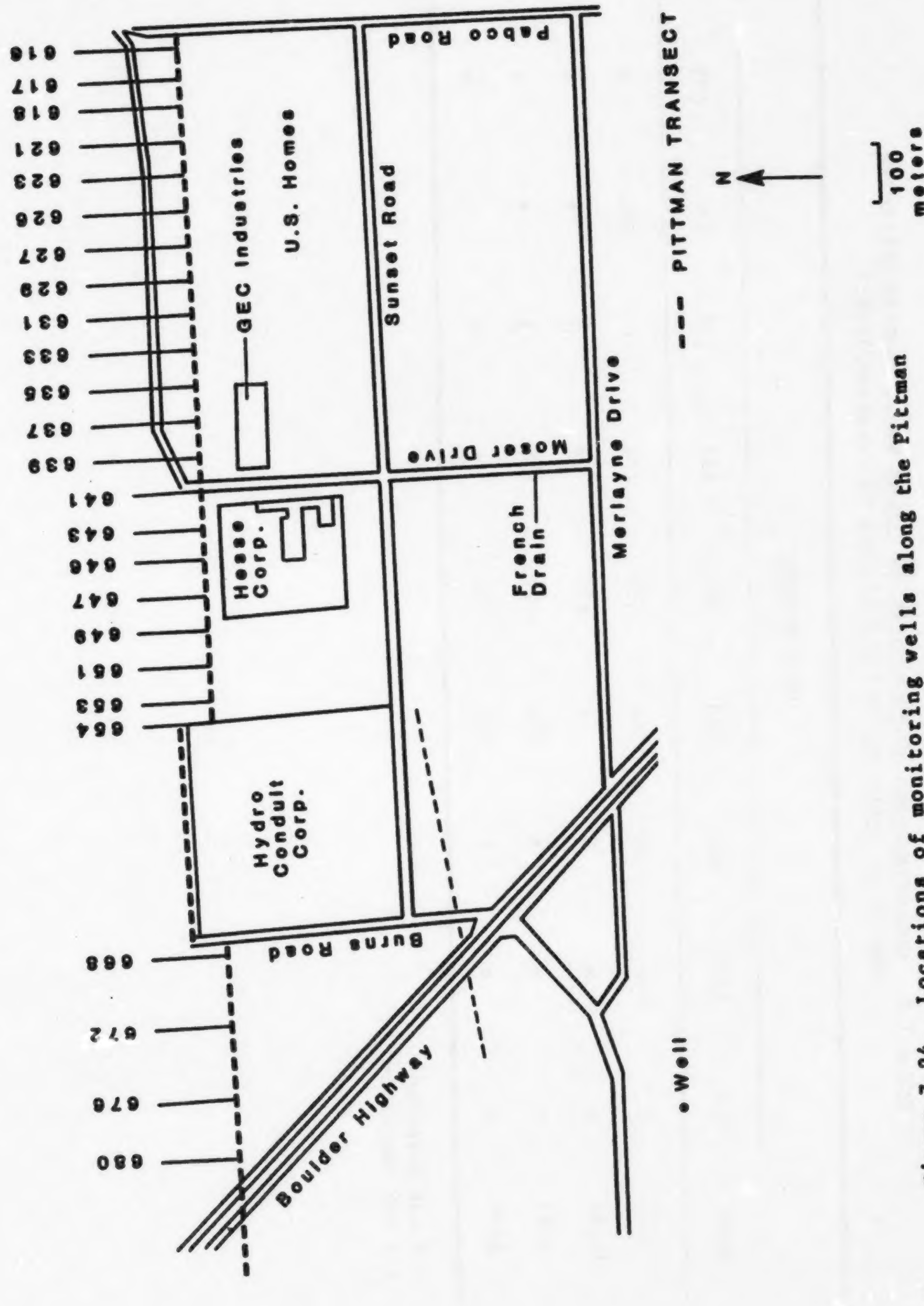

616
617
618
621
623
626
627
629
631
633
635
637
639
641
643
646
647
649
651
653
654
668
672
676
680
GEC Industries
U.S. Homes
Hesse Corp.
Hydro Conduit Corp.
Pabco Road
Sunset Road
Moser Drive
French Drain
Merlayne Drive
Burns Road
Boulder Highway
PITTMAN TRANSECT
• Well
N
100 meters

Figure 7.24. Locations of monitoring wells along the Pittman Lateral (LEMSCO, 1984).

TABLE 7.2. CONCENTRATIONS OF CHLOROFORM IN GROUND WATER SAMPLES COLLECTED FROM WELLS ALONG THE PITTMAN LATERAL (micrograms/liter)

DATE	WELL NUMBER								
	617	619	621	623	625	627	629	631	633
3/83	d	<10	28	500	430	181	11	<10	d
11/84	s	s	s	s	850	s	s	s	s
4/85	s	s	s	570	1000	175	s	s	s
8/85	s	s	s	541	732	s	s	s	s

d = not detected
s = not sampled

TABLE 7.3 CONCENTRATIONS OF BENZENE AND CHLOROBENZENE IN GROUND-WATER SAMPLES COLLECTED FROM WELLS ALONG THE PITTMAN LATERAL (micrograms/liter)

	WELL NUMBER										
DATE	633	635	637	639	641	643	645	647	649	651	653
						Benzene					
3/83	<10	340	3800	4700	3200	3400	3100	3500	1300	37	<10
11/84	s	<10	s	s	s	s	s	s	s	s	s
4/85	s	<10	s	s	5900	s	s	s	s	s	s
8/85	s	s	s	s	2548	s	3820	s	s	s	<10
						Chlorobenzene					
3/83	<10	520	4000	5100	3100	2400	4700	3600	2400	800	21
11/84	s	<10	s	s	s	s	s	s	s	s	s
4/85	s	<10	s	1300	7100	s	s	s	s	s	s
8/85	s	s	s	s	4521	s	5060	s	s	s	60

s = not sampled
a = not analyzed (sample holding time exceeded)

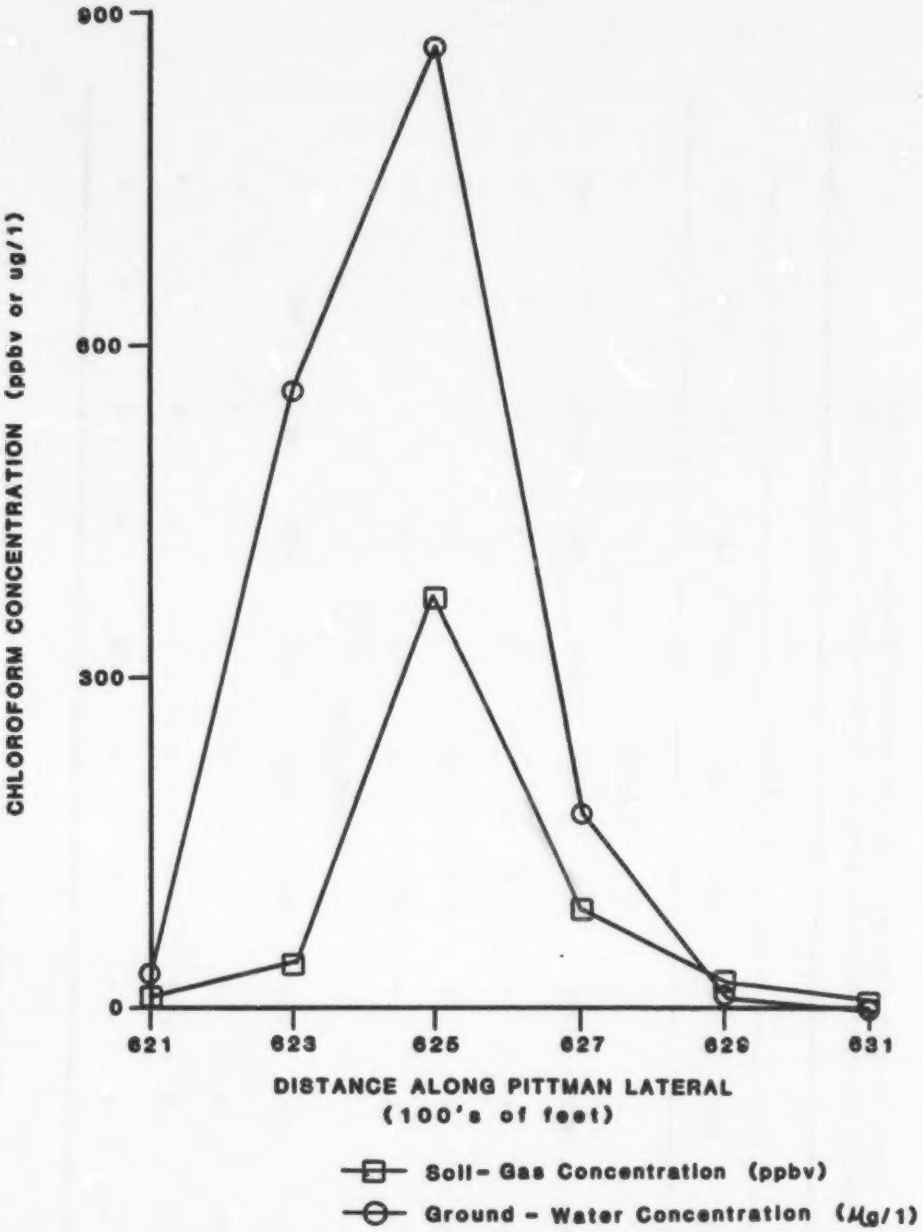


Figure 7.25. Ground-water concentrations of chloroform, benzene and chlorobenzene.

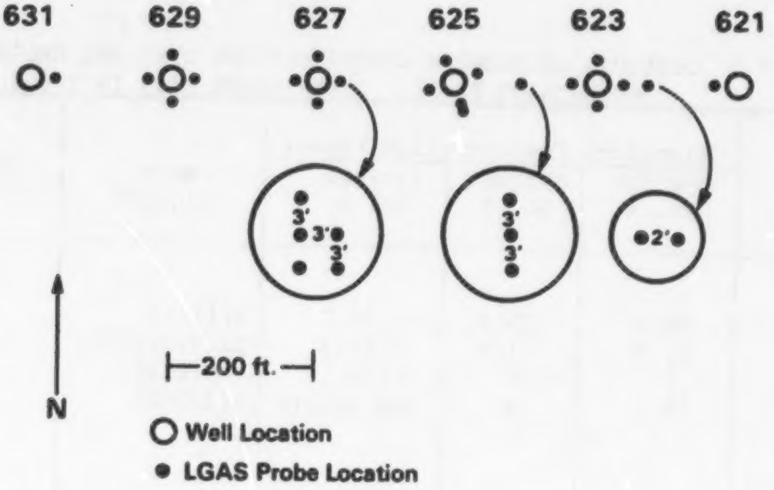

631
629
627
625
623
621
3'
3'
3'
3'
3'
2'
N
200 ft.
Well Location
LGAS Probe Location

Figure 7.26. Probe locations in the area of the chloroform/ tetrachloride.

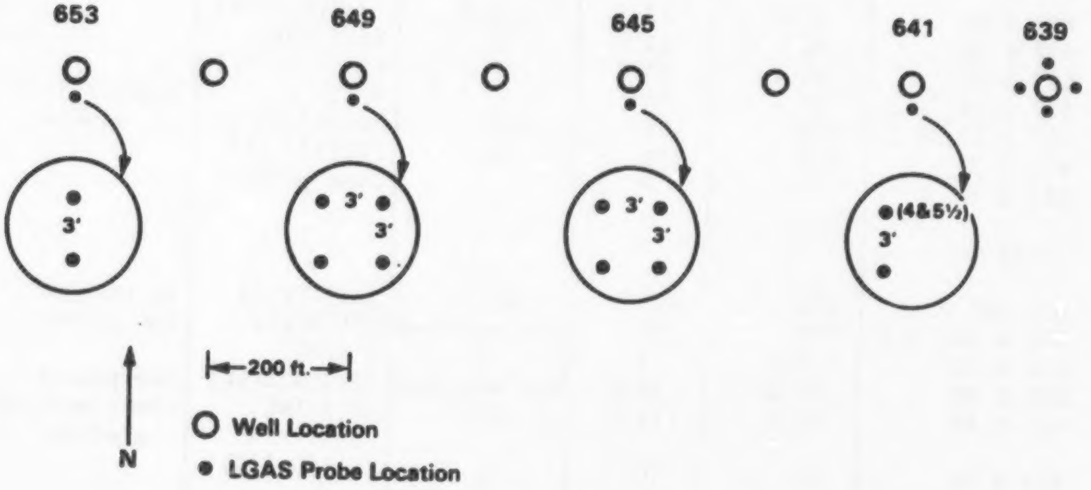

653
649
645
641
639
3'
3'
3'
3'
3'
(4&5½)
3'
N
200 ft.
Well Location
LGAS Probe Location

Figure 7.27. Probe locations in the area of the benzene/ chlorobenzene contaminant plume.

TABLE 7.4 OBSERVED CHLOROFORM CONCENTRATIONS OVER THE CHLOROFORM CONTAMINANT PLUME. DEPTH STUDY DATA IN TABLE 2.2.

Date, No. of Well, Location	Chloroform Concentration (ppbv)			mean [SD/RSD]	Comments
	Syringe No. 1	Syringe No. 2	Syringe No. 3		
7-17-85:					
623 S 20	24.9	26.2	28.9	27[2/7%]	
623 N 20	12.7	11.8	12.3	12.3[0.5/4%]	
623 W 20	119	108	117	115[6/5%]	
623 E 20	8	4	bad sample	6[3/50%]	
7-18-85:					
625 ENE 20	378.2	381.1	369.9	376[6/2%]	Sampling grid rotated 22° to avoid earlier probe locations
625 WSW 20	272.3	264.7	261.2	266[6/2%]	
625 NNW 20	330.9	313.6	332.4	326[10/3%]	
625 SSE 20	-	-	-	bad point	
7-22-85:					
627 N 20	73.0	72.7	72.9	72.9[0.1/0%]	
627 W 20	32	23	30	28[5/18%]	
627 S 20	45.4	45.8	45.4	45.6[0.2/0%]	
627 E 20, S 3	54	54	57	55[2/4%]	3 ft. x 3 ft. square
627 E 23, S 3	166	161	155	161[6/4%]	
627 E 23,	119	119	99	112[12/11%]	
627 E 20	-	-	-	bad point	
7-23-85:					
625 SSE 25	492	516	524	511[17/3%]	to replace bad points
627 E 20, N 3	171	171	not analyzed	171[0/0%]	
631 E 20	5	5	5	5[0/0%]	
623 E 40	32.2	31.9	not analyzed	32.1[0.2/1%]	two points check spatial gradient
623 E 42	32.7	24.5	22.1	27[5/19%]	
621 W 20	11	10	11	10.5[0.3/3%]	
7-24-85:					
629 W 20	12.4	8.5	9.6	10[2/20%]	
629 E 20	33.1	23.8	25.5	27[5/19%]	
629 N 20	22.3	25.3	26.6	25[2/8%]	
629 S 20	30.9	31.2	29.3	30[1/3%]	

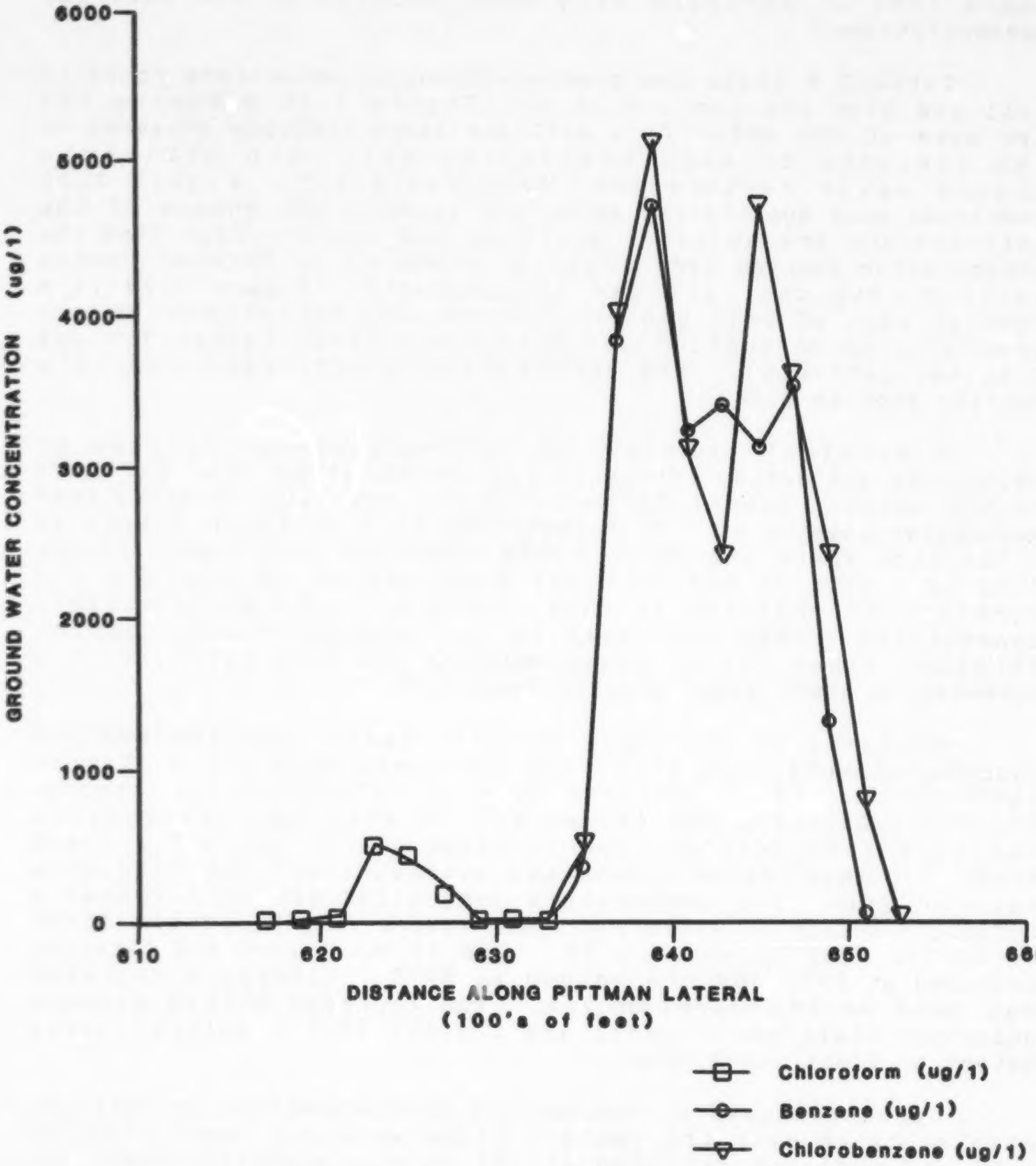


Figure 7.28. Chloroform concentrations at 4-foot depth as a function of distance across plume.

where 1000 ul syringes were used because of low soil-gas concentrations.

Table 7.4 lists the concentrations of chloroform found in soil gas over the eastern plume; Figure 7.28 compares the averages of the chloroform soil-gas concentrations measured in the vicinity of each monitoring well with available ground-water measurements from Table 7.2. Figure 7.28 indicates good qualitative agreement between the shapes of the soil-gas and ground-water profiles despite the fact that the ground-water samples were taken at times up to several months earlier than the soil-gas measurements. Figure 7.29 is a scatter plot of soil-gas chloroform concentrations versus ground-water chloroform concentrations (from Tables 7.2 and 7.4, respectively). The correlation coefficient for this scatter plot is 0.848.

A vertical profile of soil-gas concentrations of chloroform and carbon tetrachloride was obtained near Well 623 in the eastern plume; Table 7.5 lists the data obtained from successive samples at 1-foot intervals to a depth of 6 feet at a location where the water table depth was 12.5 feet. Figure 7.12 is a plot of the vertical profiles of chloroform and carbon tetrachloride at this location. Both gases exhibit essentially linear increases in concentration with depth; straight lines fit by least-squares fit both gases, with a correlation coefficient greater than 0.99.

Analysis of soil-gas samples taken over the western benzene/chlorobenzene plume was performed with two different instruments: (1) a Photovac GC with photoionization detector (Photovac GC/PID), and (2) an AID GC with photoionization detector (AID GC/PID). The Photovac GC/PID had a 5 percent SE-30, 1/8-inch Teflon column and ultrapure air was used as a carrier gas. The temperature-controlled AID GC/PID used a 6-foot, 1-8-inch ID stainless steel column with 3 percent SE-30 on 80/100 mesh Chromosorb HP. The injector port and detector operated at 89°C and the column at 82°C. Ultrapure nitrogen was used as the carrier gas. The Photovac GC/PID benzene detection limit was 1 ppbv, and the AID GC/PID chlorobenzene detection limit was 3 ppbv.

Concentrations of benzene and dichlorobenzene in soil-gas samples taken over the western plume were all less than 10 ppbv and were not detected at all in many samples. These low concentrations are unexplained although the investigators speculated that biodegradation might be responsible.

Conclusions

These two case studies illustrate the use of soil-gas measurements as a means of delineating ground-water contaminant

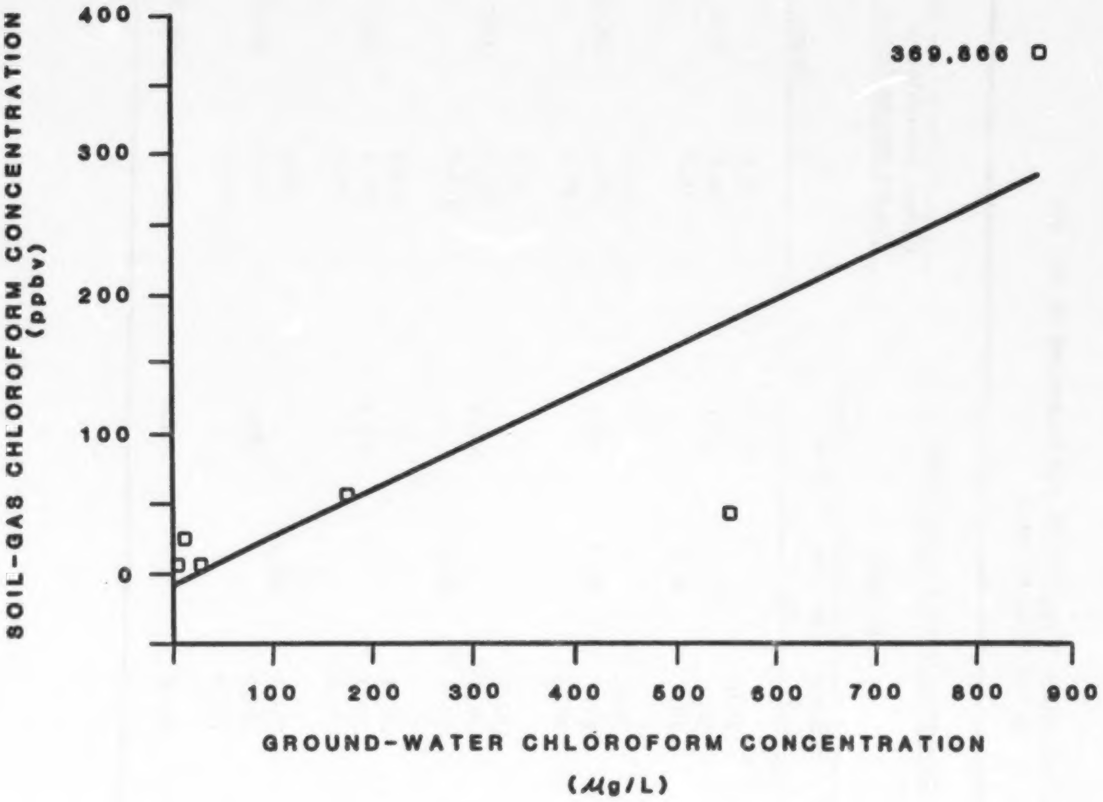


Figure 7.29. Soil-gas chloroform concentrations at 4-foot depth as a function of ground-water chloroform concentrations (r = 0.848).

TABLE 7.5 CHLOROFORM AND CARBON TETRACHLORIDE CONCENTRATIONS IN SOIL GAS AS FUNCTIONS OF DEPTH

Location (Base at No.623W100		Chloroform Concentration (ppbv)				Carbon Tetrachloride Concentrations (ppbv)	
		Measured					
	Depth (ft)	Syringe No.1	Syringe No.2	Syringe No.3	Mean		Mean
Base	1	22.9	23.0		21.2	35.7	35.6
3 ft north	1	23.5	22.3			36.0	
6 ft north	1	18.5	18.3	20.1		35.0	
Base	2	76.9	75.3		68.4	106.0	98.0
3 ft north	2	72.8	69.2	68.3		101.0	
6 ft north	2	55.4	60.2			87.0	
Base	3	109.0	110.0		105.2	145.0	142.7
3 ft north	3	111.0	110.0			149.0	
6 ft north	3	83.4	111.0	102.0		134.0	
Base	4	160.0	146.0		144.7	198.0	196.0
3 ft north	4	150.0	148.0			194.0	
6 ft north	4	122.0	142.0			196.0	
Base	5	206.0	206.0	202.0	187.4	249.0	229.0
3 ft north	5	188.0	177.0			226.0	
6 ft north	5	150.0	183.0			212.0	
Base	6	256.0	216.0		236.0	273.0	273.0

plumes. In the first study, vapors from leaked gasoline (dissolved in ground-water and possibly lying on top of the water table) moved upward through approximately 40 feet of alluvial overburden (largely sands and gravels) in concentrations large enough to be measurable at depths of about 5 feet. By sampling soil gas over the entire study area with steel probes driven to 5 feet and by analyzing the samples in the field with a transportable gas chromatograph, the lateral extent of the plume could be mapped. Not every vapor component appeared to be a good tracer of ground-water contamination; total non-methane hydrocarbons, butane, and isooctane appeared to outline a plume which was not inconsistent with that estimated from ground-water sampling. Contours drawn with ethane/propane and benzene did not resemble the ground-water plume. Benzene concentrations near the surface were so low as to be nearly unmeasurable despite substantial quantities in ground-water; this implies that some phenomenon depletes benzene from the organic vapors at some point in the migration path. The choice of tracer is therefore quite important.

In the second study, soil-gas concentrations of chloroform defined a plume of chloroform in the ground-water downgradient of a large industrial plume. Here the depth to water was about 20 feet in desert alluvium. Ground-water concentrations of benzene of 2-5 mg/l caused no measurable soil-gas concentrations of benzene. Again, benzene appears to be of little use as a tracer. Perhaps the most important result of the second study is the linear relationship between depth and soil-gas concentrations of chloroform and carbon tetrachloride in Figure 7.30. This behavior is exactly what would be expected if simple diffusion processes were the primary mechanism governing the vertical migration of the gases. Figure 7.30 lends hope that it may be possible to derive a quantitative relationship between organic concentrations in ground-water and those in soil gas, at least in some locations.

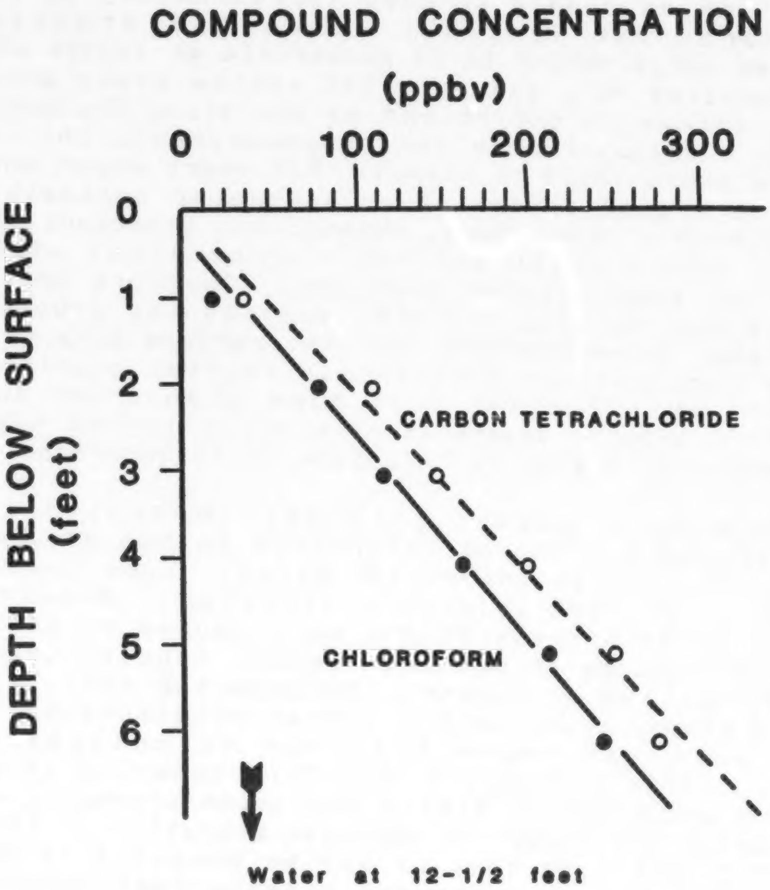


Figure 7.30. Chloroform and carbon tetrachloride depth distribution. Coefficient of determination (r^2 = .99) (Kerfoot, in draft, 1986).

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CHAPTER 8

SUMMARY AND CONCLUSIONS

UTILIZATION OF SOIL-VAPOR MEASUREMENTS

Soil-vapor measurement is a useful tool in subsurface investigations. Its most popular use is in mapping the extent of ground-water and unsaturated zone contamination related to surface spills, leaks from storage tanks, and leachates and leakage from waste disposal sites. The technique has potential application in most Superfund site investigations because many of the most frequently observed contaminants at Superfund sites are volatile organics. Volatile organics are such a common component of ground-water contamination from Superfund and interim status RCRA facilities that VOC analysis has been suggested as a detection indicator parameter for interim status RCRA monitoring.

Transport Processes

Organic liquids spilled or applied on the surface will tend to migrate downward through the vadose zone and will leave a cone of material contaminated by residual amounts of the organic. Many properties of both the organic liquid and the subsurface will influence the downward migration of the organic and its subsequent behavior, as discussed in Chapters 2 and 3. Once a low-density organic liquid has reached the water table, it will begin to create a "mound" and to spread. Behavior of each organic contaminant will be governed by its individual characteristics such as density, water solubility, and tendency to adsorb onto clays and organic constituents of soils. The low-density fluids will float on the water table and continue to spread; some fraction of the various organic components will dissolve in ground-water and move with ground-water flow as governed by Darcy's Law. Organic liquids which are immiscible in water and denser than water could sink through the saturated ground-water zone if not bound to soil as residuals.

The volatile components of the contaminant will release chemical to the vapor phase, which will then either migrate toward the soil surface by diffusion or sink through the soil air if the partial pressure of the vapor is high and the vapor is denser than air. The rate of migration will be a function of the soil resistance to vapor flow, of the amount which is redissolved into the liquid phase, and of the amount which is adsorbed or degraded. In most if not all cases, the rates of vapor migration will be much faster than rates of ground-water movement. For a situation where the dissolved components have migrated downgradient of the original spill location, initial soil vapor concentrations of the organic contaminant immediately above the water table can be predicted from Henry's Law, as discussed in Chapters 1 and 3. Chapter 1 discusses the simple situation where the organic vapor is "conservative" and is not degraded or absorbed, where the vadose (unsaturated) zone is homogeneous in composition, and where the rate of vapor loss from the surface is small compared to the aqueous concentration. An example might be a chlorinated organic solvent in a homogeneous sand. In this case theory predicts a linear decrease from the initial Henry's Law vapor concentration just above the water table to near zero concentration at the surface. As discussed in Chapter 1, field data exist which confirm this behavior in certain situations. Chapter 3 presents a solution of the slightly more complicated situation where the organic vapor undergoes first-order degradation or adsorption. These two idealized situations are probably uncommon in nature since the subsurface vertical cross-section is rarely homogeneous. In general, the least permeable layer of the vertical section will control the rate of vertical migration. The vertical profiles of gas permeability, moisture content, and soil properties will usually be hard to estimate at a particular site; thus, determination of the relationship between the vapor source (residual amounts in soil and concentrations dissolved in ground-water) and the resulting vapor concentration profiles will generally not be possible.

The fact that a mathematical expression cannot usually be written to relate soil-gas concentrations to ground-water concentrations of volatile organics does not obviate the usefulness of soil-gas surveys. Detection of volatile organics in soil vapors indicates that there is clearly a source of the organics somewhere in the subsurface, and increasing soil-gas concentrations will usually indicate increasing amounts of a substance. Mapping of soil-gas concentrations measured at uniform depth, can be useful in defining the lateral extent of subsurface contamination.

Soil-Gas Surveys

Figure 8.1 is a flowchart of the planning and execution of a soil-gas survey. Preliminary sampling is performed to determine vertical profiles of subsurface organic vapor concentrations at several locations within the site to be surveyed. A tracer gas must be chosen; selection of tracer gases for the survey is aided when prior information is

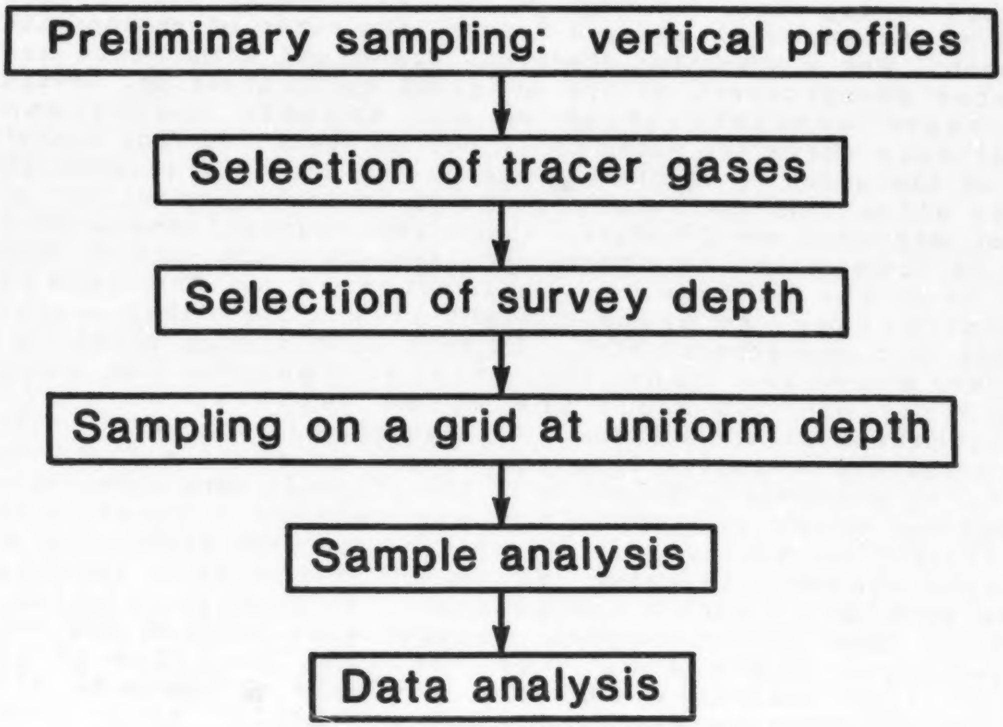
Preliminary sampling: vertical profiles
Selection of tracer gases
Selection of survey depth
Sampling on a grid at uniform depth
Sample analysis
Data analysis

Figure 8.1. Flowchart of soil-gas surveys.

available about the types and concentrations of volatile organics found in ground-water. Halogenated organics are generally preferred as tracers because they tend to be "conservative" and resistant to degradation; measurements of total hydrocarbon concentrations may also give good results. Based on the preliminary vertical profiles, a sampling depth is chosen which appears likely to provide gas concentrations large enough to be readily quantified by available analytical techniques. Soil-gas samples are then collected over the survey area on a predetermined grid at the uniform sampling depth. The samples are analyzed on site or are transported to a laboratory for analysis. Data analysis consists of plotting the values on a map of the survey area and drawing isoconcentration lines either by hand or with a computer algorithm. The final objective of the soil-gas survey will be the siting of monitoring wells to obtain representative measurements of ground-water concentrations of the contaminants or to obtain core samples to determine the concentrations of the contaminants in the soils.

Sampling Devices

Figure 8.2 is a schematic of the sampling and analysis process. Soil vapor samples are obtained with any of several methods. The available methods include headspace measurements, ground probes, flux chamber measurements, and passive sampling. While any of these techniques may be used to detect subsurface hydrocarbon contamination, they are not equivalent. The ground probe and headspace measurement techniques measure a soil-gas concentration, the flux chamber technique measures an emission rate, and the passive sampling technique measures some function of an average soil-gas concentration. The technique chosen will depend on study objectives, on the magnitude of soil hydrocarbon vapor concentrations, and on the sensitivity of available analytical instrumentation. The flux chamber is generally appropriate for applications where a measure of human exposure is to be determined and where soil-gas concentrations are relatively large because the introduction of sweep air effectively dilutes the organic vapor concentrations. The passive sampling techniques serve to integrate soil-gas concentrations over some period of time and could be of use where detection of very low concentrations is necessary. Ground probes are probably the most widely used technique because of speed and cost. Headspace measurements can be used in preliminary surveys to monitor concentrations in monitoring wells, storm sewers, utility vaults, or other subsurface structures, and as a first step in planning more extensive investigations. The technique can also be used to measure headspace concentrations of organic vapors in containers holding soil core samples; this approach has been used to

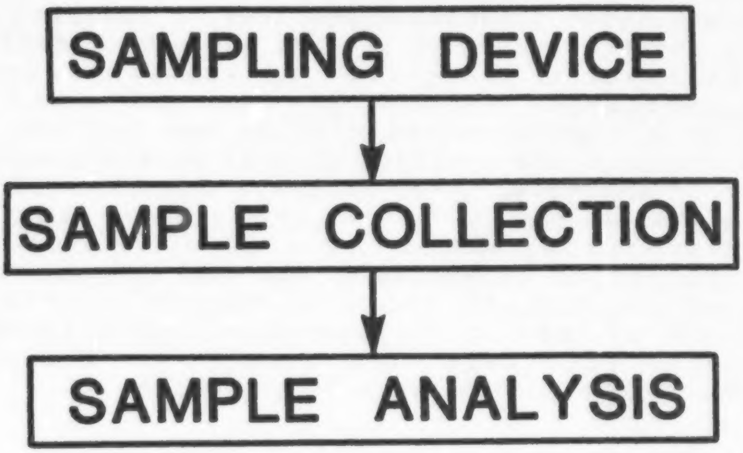
SAMPLING DEVICE
SAMPLE COLLECTION
SAMPLE ANALYSIS

Figure 8.2. Flowchart of soil-gas measurements.

provide vertical profiles of relative organic vapor concentrations.

Sample Collection

Accurate determination of the concentration and composition of organic compounds in soil gas usually requires the collection of samples which are subsequently analyzed in a laboratory where conditions are sufficiently stable to permit GC analysis. Analysis may take place in a mobile field laboratory or in a sophisticated modern analytical laboratory at considerable distance from the site. In either case, a representative sample must be collected, and its integrity must be maintained until it can be analyzed. The sampling technique must be compatible with the analytical method. Relatively insensitive analytical methods require large samples. Long sample transport distances require rugged sample containers. Sample collection methods for VOCs in gases can be divided into two classes:

- adsorbent methods where the gas is passed through a solid adsorbent which removes the VOCs from the inorganic gas matrix; and
- whole-air methods in which the entire sample is placed in a container and transported to the laboratory.

Adsorbent materials most often used for VOCs are activated charcoal and porous polymers such as Tenax. Other adsorbents which have been used are molecular sieves, silica gel, and activated alumina. The adsorbent method is attractive because it concentrates the gas components of interest and removes many of the components known to add to the instability of the sample and to interfere with the sample analysis. The adsorbents are small and can be easily transported to and from the field. The limitation of the adsorbent methods are possible irreversible adsorption, incomplete adsorption, and artifact formation. Irreversible adsorption occurs when adsorbed components cannot be completely desorbed. Incomplete adsorption is also called breakthrough and results in the loss of the more volatile sample components. Artifact formation can occur during thermal desorption or from reaction of the sample with the adsorbent material. All three of these possible problems must be fully investigated during sample method validation.

Collection of whole-air samples is probably the most widely used technique in soil-gas investigations. In selecting an appropriate container, the investigator should consider the length of time which the samples must be held in the container, the need for ruggedness if the samples are to be shipped long distances, and the ability to clean the container between samples. Three different classes of containers have been used in such investigations:

- plastic bags made of Tedlar or Teflon;
- passivated stainless-steel cannisters and syringes; and
- glass syringes.

Tedlar and Teflon bags are convenient and inexpensive. However, photochemical reactions can degrade samples if the bags are exposed to light; sample leakage during transport can occur; and gas species can permeate into the bags and out of the bags during transport and storage. Consequently, plastic bags are not recommended for soil-gas surveys unless storage times are short, and concentrations are high.

Passivated stainless-steel cannisters are sturdy and impervious to light, and they can be cleaned easily. Samples can be held for periods up to several days in properly prepared cannisters. Stainless-steel syringes are on the market which should have the same advantages as the cannisters. However, such devices are expensive and represent a considerable investment.

Glass containers such as syringes have also been used to collect gas samples. However, glass containers usually require Teflon valves and seals which can be a source of contamination. Because glass transmits light, they should be kept out of direct sunlight to avoid photochemical reactions in the samples. Because of their fragility, such vessels are most appropriate for on-site use. Glass syringes are the most popular devices for collection of soil-gas samples when on-site analysis is planned.

Sample Analysis

Analytical methods typically used in soil-gas surveys include portable VOC analyzers, field gas chromatographs, and laboratory-based GCs. The method chosen to analyze soil-gas samples depends on the pollutant being monitored, the concentrations of respective pollutant species, and the information to be obtained from the analytical results. Expected concentrations for organic species in soil gas can range from the pptv level (below most analytical detection limits) in background measurements to several per cent by volume in measurements made directly over a liquid lens of a highly volatile organic fluid such as gasoline. The concentration level actually measured will depend on the sampling method used and on the degree of dilution (as in flux chambers) or concentration (as in charcoal or Tenax adsorption devices). More sensitive methods may be needed at plume fringes than at locations near the source. Some of the considerations involved in selecting the appropriate analytical technique(s) are

- the need for detailed chemical speciation;
- the need for relative values or absolute concentrations;
- the need for on-site analyses;
- the methods of sample collection

Portable VOC analyzers can be useful at sites where total hydrocarbon concentrations are greater than 1 ppmv. Such concentrations are not uncommon at leaking gasoline storage tanks and gasoline spill sites. Portable VOC analyzers can be particularly convenient when used in conjunction with driven ground probes to sample directly from the probes. The advantages of portable VOC analyzers are the elimination of sample collection and transport; their major disadvantages are calibration problems, the need for large sample volumes, and lack of sensitivity.

Gas chromatography is used where concentrations less than 1 ppmv must be measured or where chemical speciation is needed. Detection methods used for GC analysis of soil-gas samples include:

- flame ionization detector (FID) for volatile hydrocarbons;
- photoionization detector (PID) for aromatic hydrocarbons and sulfur species;
- electron capture detector (ECD) for halogenated hydrocarbons;
- Hall electroconductivity detector (HECD) for detection of halogenated species, nitrogen-containing organics, or sulfur-containing species;
- flame photometric detector (FPD) for sulfur and phosphorous compounds.

Field gas chromatographs are used where samples can be collected and analyzed on site. The simplest field instruments are portable VOC analyzers with chromatographic options such as the Photovac equipped with a PID and the Century OVA equipped with a FID. The useful detection limits for such instruments are usually on the order of 1 ppmv. A step above the "portable" GCs are the "field" GCs: small, sturdy GCs with temperature-controlled ovens and a variety of injectors and detectors. Best results are obtained with instruments with heated-gas sampling valves for injection of the gas samples. The detectors most commonly found are the FID, PID, and the ECD. The ECD is quite sensitive, with detection limits for halogenated compounds in the ppbv range.

Soil-gas samples will need to be sent to an off-site laboratory when positive chemical species identification is required, when very low detection limits are required, when difficult sample matrices are encountered, or when environmental conditions prohibit on-site analysis. Combinations of detector types in multi-detector systems are useful for specific types of analyses. Mass spectrographs can be used where positive identification of chemical species is otherwise difficult. Modern analytical laboratory methods are readily available with the capability to separate and quantitate VOCs in soil gas at concentrations less than 1 ppbv and to identify gas species with high confidence. The investigator's task is to choose a level of sophistication which accomplishes the survey objectives at a reasonable cost.

Quality Assurance and Quality Control

The desired product of most soil-gas surveys is a contour map of soil-gas concentrations, in either two or three dimensions. The investigator usually intends to use the contoured soil-gas measurements as a surrogate for other more expensive measurements such as ground-water or soil residual concentrations. The important factors are the location and shape of the contours and their relative magnitudes, not their absolute concentrations. However, individual measurements must be comparable to one another in order to draw the contours. To insure comparability, a soil-gas survey, like any other environmental measurements program, needs a quality assurance/quality control program. EPA policy requires a written QA/QC plan for any environmental measurements program. The QA/QC plan should address the sampling method, the analytical method, and the data reduction and reporting steps. Discussion of analytical QA/QC should include method calibration and primary and field standards. Duplicate analyses and samples are necessary to determine the variability of the sampling and analytical techniques. Blank analyses are required to determine the level of contamination attributable to the sampling method and to the analytical method. To determine the absolute accuracy and lab-to-lab variability, audit sample analysis and interlaboratory comparison studies are required.

Data Analysis

Another useful step in assuring that measurements are comparable is a components of variance analysis, a statistical procedure which develops a model to assess the error in reported concentrations attributable to each step in the sampling and analysis process.

Data analysis for soil-gas surveys usually involves interpolation between sample points and the drawing of contours. Because soil-gas measurements represent concentrations of certain gas species near the surface, they do not necessarily represent the concentrations of the compounds in an underlying area of soil contamination or of ground-water plume (or a consistent or "monotone" transformation of those concentrations). Under the best of conditions, soil-gas measurements represent a monotone transformation distorted by measurement errors of the concentrations of the compounds in soil or ground-water below the point of measurement.

Many methods of interpolation between data points are available to the investigator, such as linear, inverse squared distance, splines, and kriging. Most such methods are deterministic and do not rely on a probability model while kriging does need such a model. The various common interpolation methods typically give similar results concerning the general pattern of soil-gas contours (which is the final objective of a survey). Kriging has the advantage that it provides an estimated standard error for each interpolation. However, the estimated standard error in kriging is highly dependent on the probability model which must be developed again for each new survey because each site is unique. Good estimation of a model requires more and better data than are usually available from a soil-gas survey. For this reason, use of a simple spline or inverse-square interpolation procedure is probably more efficient. If an estimate of the interpolation error is desired, procedures other than kriging can be employed.

Care must be used in employing computer interpolation and contouring packages. Such packages are ill-equipped to deal with situations where adjacent data points differ by several orders of magnitude. Such situations are not uncommon in soil gas data but do not necessarily represent corresponding changes in the variables of ultimate concern (soil or ground-water concentrations). Because such large isolated values are likely to represent anomalies as enhanced gas-flow paths, it would be better to simply flag these values rather than to incorporate them into the interpolation process.

Case Studies

The two case studies presented here illustrate the use of soil-gas measurements as a means of delineating ground-water contaminant plumes. In the first study, vapors from leaked gasoline (dissolved in ground-water and possibly lying on top of the water table) moved upward through approximately 40 feet of alluvial overburden (largely sands and gravels) in concentrations large enough to be measured at depths of about 5 feet. By sampling soil gas over the entire study area with steel probes and by analyzing the samples in the field with a transportable gas chromatograph, the lateral extent of the plume could be mapped. Not every vapor component appeared to be a good tracer of ground-water contamination. The choice of tracer is therefore quite important.

In the second study, soil-gas concentrations of chloroform defined a plume of chloroform in ground-water which was downgradient of a large industrial plume. The most important result of the second case study is probably the observed linear relationship between depth and soil-gas concentrations of chloroform and carbon tetrachloride which would be expected if simple diffusion processes were the primary mechanism governing the vertical migration of the gases. This case study lends hope that it may be possible to derive a quantitative relationship between organic concentrations in ground-water and those in soil gas, at least for some gas species and at some locations.

Both case studies involved the use of other methods to support the data that were obtained from the soil-gas methods. Geophysics and hydrogeologic information from existing wells in the vicinity of the soil-gas surveys were useful in the design of the survey and the interpretation of the results. Like any step in a ground-water study soil-gas measurements by themselves are a useful but not exclusive means for defining the extent of ground-water contamination from organics.